Symmetry, space, stars and C_{60}*

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INTRODUCTION. A SUMMARY OF THE KEY PHASES IN THE BIRTH OF THE FULLERENES

The story of the discovery of C_{60}, Buckminsterfullerene, Fig. 1, and the birth of Fullerene Science consists of several disparate strands which came together over ten days in September 1985. During this period of feverish activity, working with Jim Heath, Sean O'Brien, Yuan Liu, Bob Curl and Rick Smalley at Rice University in Texas, evidence was found that a C_{60} molecule self-assembled spontaneously from a hot nucleating carbon plasma (Kroto, Heath, *et al.*, 1985). The molecule had, however, a prehistory: The earliest paper which describes the C_{60} molecule is to be found in Kagaku (in Japanese), where Eiji Osawa in 1970 suggested that it should be stable (Osawa, 1970,1971) and the following year discussed its possible aromatic properties in more detail in a book with Yoshida (Yoshida and Osawa, 1971). Bochvar and Gal'pern published a theoretical study in 1972 (Bochvar and Gal'pern, 1973; see also Stankevich *et al.*, 1984). Somewhat earlier, in 1966, David Jones had conjectured that if pentagonal disclinations could be introduced among the hexagons in a graphene sheet, the sheet would close into a hollow balloon (Jones, 1966, 1982). We, however, did not know about this prehistory and none of us had ever heard of such a molecule or thought about it.

In retrospect, as far as I was concerned, I seem to have been fascinated by various peculiar aspects of carbon chemistry for much of my research career. With the perspective of hindsight my involvement can be split into five phases: At Sussex, in the late 1960s, David Walton and I initiated a synthetic/spectroscopic study (Phase I) which led directly—in the mid 1970s—to some unexpected discoveries (with collegues at Sussex and NRC Ottawa, Canada) of long carbon chain molecules in the interstellar medium (Phase II). At about this time Don Huffman and Wolfgang Krätschmer were developing laboratory experiments which focused on the composition of the particulate carbon material which occupies the same interstellar regions—indeed, the agents which caused the scattering in the dark regions—and observed some intriguing new unexplainable features in the 220-nm region of their laboratory data. Also at about this time Richard Smalley was developing a range of advanced chemical physics techniques which culminated in an ingenious apparatus which enabled small clusters of *refractory* materials to be created and probed for the first time. This was the pulsed supersonic nozzle–laser vapourisation apparatus (Dietz *et al.*, 1981). It is my view that the *raison d'etre* of this machine was to discover C_{60}.

It was the marriage of ideas resulting from the discoveries of carbon chains in space with the recognition that the cluster beam technique might offer laboratory support for their circumstellar origin that in 1985 resulted in the serendipitous discovery that the C_{60} molecule not only existed but that it self-assembled (Phase III) (Kroto, Heath, *et al.*, 1985; Kroto, Allaf, and Balm, 1991). After this revelation it still remained for unequivocal proof of the soccerball structure to be obtained (Phase IV). Several groups made important contributions: (i) theoreticians, who had a field day and came up with some results which ultimately proved crucial for the extraction (Weltner and Van Zee, 1989; Kroto, Allaf, and Balm, 1991); (ii) the Rice group (initially in collaboration with Sussex; Heath *et al.*, 1987; Curl and Smalley, 1988; Kroto, Allaf, and Balm, 1991); (iii) the Sussex group (Kroto, 1988, Kroto, Allaf, and Balm, 1991); (iv) the IBM group (Meijer and Bethune, 1990); and last but not least; (v) the Heidelberg/Tucson group, which succeeded in the first extraction of macroscopic quantities (Krätschmer, Lamb, *et al.*, 1990; Krätschmer, Fostiropoulos, and Huffman, 1990a, 1990b). It was this fantastic breakthrough that has made the explosive growth of Fullerene Science possible (Phase V). The advance made by Krätschmer and Huffman and their students is one of the most beautiful pieces of fundamental science.

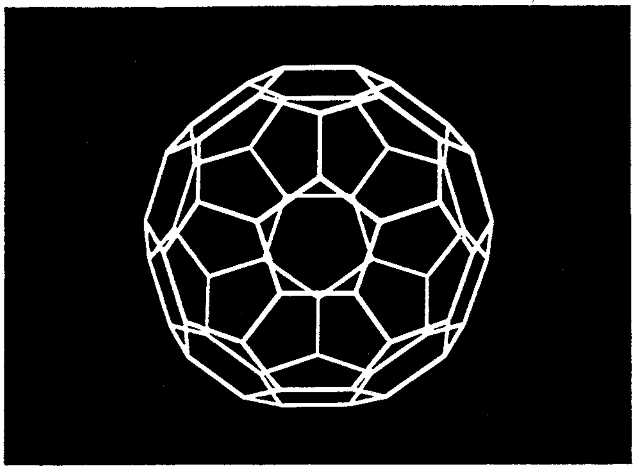

FIG. 1. C_{60} Buckminsterfullerene (Kroto, Heath, *et al.*, 1985).

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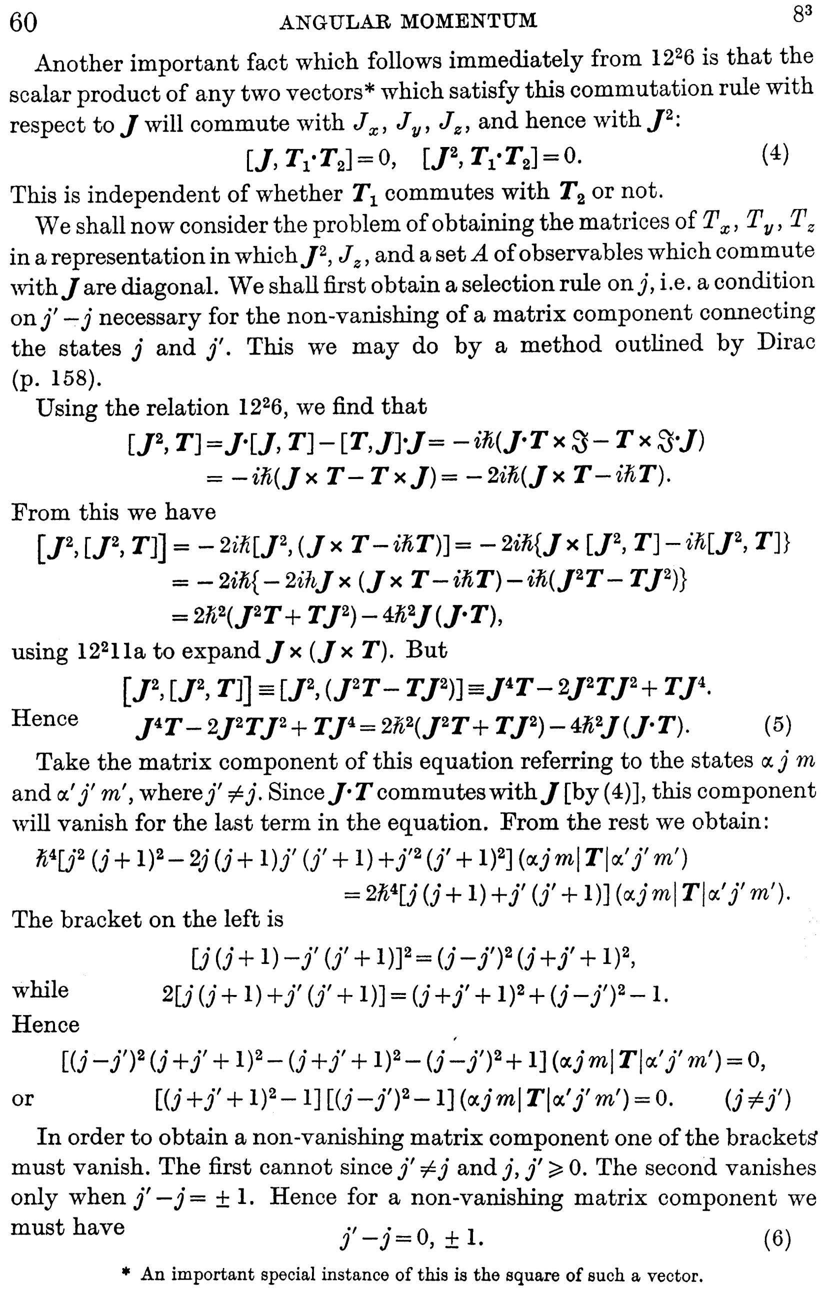
*The 1996 Nobel Prize in Chemistry was shared by Robert Curl, Harold Kroto, and Richard Smalley. This lecture is the text of Professor Kroto's address on the occasion of the award.



60 ANGULAR MOMENTUM 8^3

Another important fact which follows immediately from 12^26 is that the scalar product of any two vectors* which satisfy this commutation rule with respect to $\boldsymbol{J}$ will commute with J_x, J_y, J_z, and hence with $\boldsymbol{J}^2$:

$$[\boldsymbol{J}, \boldsymbol{T}_1 \cdot \boldsymbol{T}_2] = 0, \quad [\boldsymbol{J}^2, \boldsymbol{T}_1 \cdot \boldsymbol{T}_2] = 0. \tag{4}$$

This is independent of whether $\boldsymbol{T}_1$ commutes with $\boldsymbol{T}_2$ or not.

We shall now consider the problem of obtaining the matrices of T_x, T_y, T_z in a representation in which $\boldsymbol{J}^2$, J_z, and a set A of observables which commute with $\boldsymbol{J}$ are diagonal. We shall first obtain a selection rule on j, i.e. a condition on $j'-j$ necessary for the non-vanishing of a matrix component connecting the states j and j'. This we may do by a method outlined by Dirac (p. 158).

Using the relation 12^26, we find that

$$\begin{aligned}[\boldsymbol{J}^2, \boldsymbol{T}] &= \boldsymbol{J} \cdot [\boldsymbol{J}, \boldsymbol{T}] - [\boldsymbol{T}, \boldsymbol{J}] \cdot \boldsymbol{J} = -i\hbar(\boldsymbol{J} \cdot \boldsymbol{T} \times \mathfrak{J} - \boldsymbol{T} \times \mathfrak{J} \cdot \boldsymbol{J}) \\ &= -i\hbar(\boldsymbol{J} \times \boldsymbol{T} - \boldsymbol{T} \times \boldsymbol{J}) = -2i\hbar(\boldsymbol{J} \times \boldsymbol{T} - i\hbar \boldsymbol{T}).\end{aligned}$$

From this we have

$$\begin{aligned}\big[\boldsymbol{J}^2, [\boldsymbol{J}^2, \boldsymbol{T}]\big] &= -2i\hbar[\boldsymbol{J}^2, (\boldsymbol{J} \times \boldsymbol{T} - i\hbar\boldsymbol{T})] = -2i\hbar\{\boldsymbol{J} \times [\boldsymbol{J}^2, \boldsymbol{T}] - i\hbar[\boldsymbol{J}^2, \boldsymbol{T}]\} \\ &= -2i\hbar\{-2i\hbar\boldsymbol{J} \times (\boldsymbol{J} \times \boldsymbol{T} - i\hbar\boldsymbol{T}) - i\hbar(\boldsymbol{J}^2\boldsymbol{T} - \boldsymbol{T}\boldsymbol{J}^2)\} \\ &= 2\hbar^2(\boldsymbol{J}^2\boldsymbol{T} + \boldsymbol{T}\boldsymbol{J}^2) - 4\hbar^2\boldsymbol{J}(\boldsymbol{J} \cdot \boldsymbol{T}),\end{aligned}$$

using 12^211a to expand $\boldsymbol{J} \times (\boldsymbol{J} \times \boldsymbol{T})$. But

$$\big[\boldsymbol{J}^2, [\boldsymbol{J}^2, \boldsymbol{T}]\big] \equiv [\boldsymbol{J}^2, (\boldsymbol{J}^2\boldsymbol{T} - \boldsymbol{T}\boldsymbol{J}^2)] \equiv \boldsymbol{J}^4\boldsymbol{T} - 2\boldsymbol{J}^2\boldsymbol{T}\boldsymbol{J}^2 + \boldsymbol{T}\boldsymbol{J}^4.$$

Hence

$$\boldsymbol{J}^4\boldsymbol{T} - 2\boldsymbol{J}^2\boldsymbol{T}\boldsymbol{J}^2 + \boldsymbol{T}\boldsymbol{J}^4 = 2\hbar^2(\boldsymbol{J}^2\boldsymbol{T} + \boldsymbol{T}\boldsymbol{J}^2) - 4\hbar^2\boldsymbol{J}(\boldsymbol{J} \cdot \boldsymbol{T}). \tag{5}$$

Take the matrix component of this equation referring to the states $\alpha\, j\, m$ and $\alpha'\, j'\, m'$, where $j' \neq j$. Since $\boldsymbol{J} \cdot \boldsymbol{T}$ commutes with $\boldsymbol{J}$ [by (4)], this component will vanish for the last term in the equation. From the rest we obtain:

$$\begin{aligned}&\hbar^4[j^2(j+1)^2 - 2j(j+1)j'(j'+1) + j'^2(j'+1)^2](\alpha j m|\boldsymbol{T}|\alpha' j' m') \\ &\qquad = 2\hbar^4[j(j+1) + j'(j'+1)](\alpha j m|\boldsymbol{T}|\alpha' j' m').\end{aligned}$$

The bracket on the left is

$$[j(j+1) - j'(j'+1)]^2 = (j-j')^2(j+j'+1)^2,$$

while

$$2[j(j+1) + j'(j'+1)] = (j+j'+1)^2 + (j-j')^2 - 1.$$

Hence

$$[(j-j')^2(j+j'+1)^2 - (j+j'+1)^2 - (j-j')^2 + 1](\alpha j m|\boldsymbol{T}|\alpha' j' m') = 0,$$

or

$$[(j+j'+1)^2 - 1][(j-j')^2 - 1](\alpha j m|\boldsymbol{T}|\alpha' j' m') = 0. \qquad (j \neq j')$$

In order to obtain a non-vanishing matrix component one of the brackets must vanish. The first cannot since $j' \neq j$ and $j, j' \geqslant 0$. The second vanishes only when $j'-j = \pm 1$. Hence for a non-vanishing matrix component we must have

$$j'-j = 0, \pm 1. \tag{6}$$

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* An important special instance of this is the square of such a vector.

FIG. 2. P60 of Condon and Shortley's book (1967) in which Dirac's elegant derivation of the fundamental selection rule on j, the angular momentum quantum number, is derived (published by permission of Cambridge University Press). These relations not only describe a beautiful example of the way Nature behaves but also are an exquisite example of man's mathematical invention to describe the behaviour, as well as an elegant example of typeface which visually evokes a powerful feeling for the underlying abstract concept. Buried deep in this derivation are fundamental laws of symmetry which govern the way in which light interacts with matter. These relations govern the origin of the sunlight falling on this page, the modulation of that light by the page and the print on it, and the way in which the receptors in your eye detect the reflected light and transform it into perceived images in your brain. By the way, it may be worth noting that not only does this paper consist mainly of carbon but so also does the ink.

In any complex story, the events can only be understood by reference to the complete set of personal subjective accounts of the participants—even purportedly objective accounts must be treated with skepticism (Kurosawa, 1987). In this case *all* the scientists—including research students—played crucial roles in the story. This article describes parts of the story to which Sussex researchers made contributions. There have now been numerous accounts ranging from the personal articles (Smalley, 1991; Kroto, 1992a; Curl and Smalley, 1991; Krätschmer and Huffman, 1993) to books by Baggott (1994), Aldersey-Williams (1995), Krätschmer and Schuster (1996), Dettman (1994), and Ball (1994). An excellent text focusing on the chemistry is that by Hirsch (1994). Several compendia have been published. Those edited by or with Sussex researchers include one with a historical perspective (Kroto and Walton, 1993), a second from the viewpoint of carbon materials and physics (Kroto, Cox, and Fischer, 1993) and a third which concentrates on fullerene chemistry (Taylor 1995). It should also be recognised that the discovery of C_{60} led to a further amazing advance—this was the discovery by Iijima that carbon nanotubes also form at the same time as C_{60} (Iijima, 1991).

The story of C_{60} also cannot be recounted without reference to its beauty, which results from the incredible symmetry. Another important aspect of the molecule's aura lies in the name Buckminsterfullerene (Nickon and Silversmith 1987) and the direct association it has with the geodesic domes designed by Buckminster Fuller (Marx, 1960; Fuller, 1983;Baldwin, 1996). It invests this elegant molecule with a charisma that has fascinated scientists, delighted lay people, and infected children with a new enthusiasm for science, and in particular it has given chemistry a new lease of life (Kroto, 1994).

PROLOGUE. SYMMETRY, THE KEY TO THE THEORY OF EVERYTHING

Symmetry appears to be fundamental to our perception of the physical world and it also plays a major role in our attempts to explain everything about it. As far as structural symmetry is concerned it goes back to ancient times, as indicated by the (pre-)Platonic structures exhibited in the Ashmolean Museum in Oxford (Critchlow, 1979; Lawler, 1982). The most famous examples are of course to be found in *The Timaeus*, where in the section relating to ''The Elements'' Plato says: ''In the first place it is clear to everyone (!) that fire, earth, water and air are bodies and all bodies are solids'' (!!) (Plato, ca. 300 B.C.). Plato goes on to discuss chemistry in terms of these elements and associates them with the four Platonic solids (only four at that time—until Hippasus discovered the fifth, the dodecahedron).

Although this may at first sight seem like a somewhat naive philosophy it indicates a very deep understanding of the way Nature actually functions. A curiously close contemporary analogue of this ancient assumption is to be found in the historically important article by Van Vleck (1951) on which almost all of modern molecular spectroscopy is based: Van Vleck says ''Practically everyone (!) knows that the components of total angular momentum (N.B. the angular momentum operator is usually denoted by the symbol **J** and the associated quantum number of j) of the molecule relative to the axes X, Y, Z fixed in space satisfy the commutation relation of the form

$$J_X J_Y - J_Y J_X = iJ_Z. \tag{1}$$

Klein discovered the rather surprising fact that when total angular momentum is referred to axes mounted in the molecule which we will denote by x, y, z the sign of i in the commutation relation is reversed, i.e.,

$$J_x J_y - J_y J_x = -iJ_z.\text{''} \tag{2}$$

Does practically everyone know this? I wondered whether to check this claim out by asking everyone on the main street in Brighton whether they did. I hardly knew—or more accurately, really understood—the first relation, let alone the second. However, I did know that angular momentum was quantised and governed by the fundamental relations

$$\langle j|\mathbf{J}^2|j\rangle = \hbar^2 j(j+1), \tag{3}$$

$$M_J = -j \ldots +j, \tag{4}$$

which means that J has $2j+1$ possible orientations, and

$$\Delta j = 0, \pm 1, \tag{5}$$

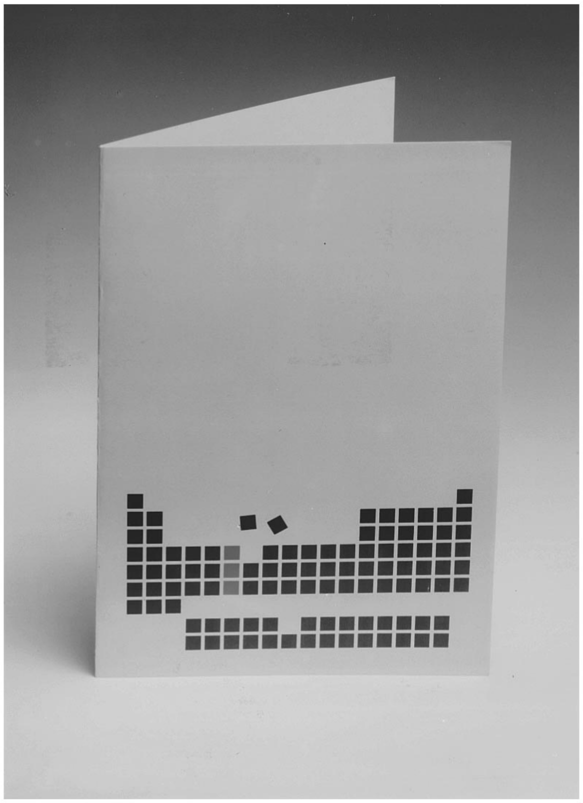


FIG. 3. This item was designed by the author for a conference. It is left to the reader to deduce the topic of the conference and also the nature of item depicted. The answers may be in *The Hitchiker's Guide to the Galaxy*.

which indicates that when a transition occurs, j may only change by one unit or on occasion remain unchanged.

I knew that the row structure of Mendeleef's periodic table could be explained on the basis of these quantum properties of angular momentum, in particular the fact that a system with angular momentum j possesses $2j+1$ quantised orientations. I decided I ought to understand these and under the tutelage of Jon Hougen and Jim Watson I dived into the ''Theory of Atomic Spectra'' of Condon and Shortley (1967). There can surely be no more elegant printed page in the Sciences or the Arts than page 60 of this book, Fig. 2, where Dirac's proof of the $\Delta j = \pm 1$ selection rule (it is noncommittal on $\Delta j = 0$) is presented—a perfect example of elegant and powerful use of roman typeface. One only has to look at this page to know that it must be important. As far as I was concerned it planted the desire to understand the embedded theory. The effort was (for me) considerable, but worth it and remains one of the most intellectually rewarding tasks I have undertaken. Having finally grasped the implications of these relations, I ended up writing a book called *Molecular Rotation Spectra* Kroto (1992b), which deals with the way the angular momentum relations govern the rotational dynamics of molecules.

The geometric pattern of the periodic table, Fig. 3, is an implicit result of the angular momentum description of atoms and electrons [together with a few odds and ends (!) such as the Pauli exclusion principle]. Any intelligent life on another planet that had developed an understanding of chemistry would almost certainly recognise it. The electron angular momentum wave functions are described in terms of spherical harmonics—known by mathematicians long before 1925 when Quantum Mechanics was created—and thus these symmetric mathematical functions lend an elegant beauty to the abstract description of rotational/orbital motion in atoms and molecules. Thus we discover that symmetry principles underpin the elegant quantum-mechanical description of atoms and molecules in an abstract picture in which statics and dynamics are paradoxically conflated in a way that often leaves us hovering on the boundary between abstract mathematical understanding and literal physical misunderstanding. It is the existence of similar abstract aspects of symmetry that has invested the C_{60} molecule with a charismatic quality that few other molecules possess.

PHASE I. CARBON, STILL CRAZY AFTER ALL THESE YEARS

Carbon is really peculiar—in fact, the fact that there is enough carbon around in the Universe to allow enough biology to occur and result in the Human Race at all is due to peculiarities in the nuclear chemistry of carbon. the "molecular" chemistry of carbon is no less peculiar. Even if we discount the whole of Organic Chemistry, the Inorganic Chemistry of carbon is also amazing. I worked with carbon containing species right from the start when I was a graduate student with Richard Dixon at Sheffield. My first (successful) research project was a study of the electronic spectrum of the diatomic free radical CBr in which we also explored the intrinsic nature of the bond that the carbon atom formed with halogens (Dixon and Kroto, 1963). Even more interesting was a preliminary (aborted) study of the fascinating molecule carbon suboxide OCCCO. The most interesting aspect of this molecule was the fact that it did not seem to know whether it wanted to be a linear or bent. The triatomic molecule C_3 was no less odd, exhibiting similar structural schizophrenia. The identification of C_3 in comets and flames, in the elegant historical study by Alec Douglas (1951), was a landmark in spectroscopy which added to the ubiquitous charismatic attraction of carbon species on earth as well as in space.

When I arrived at Sussex in 1967, after two years at NRC (Ottawa) and a year at Bell Labs (Murray Hill) I set up a microwave spectroscopy research programme which aimed at the creation of new molecules which contained multiple bonds between carbon and various second- or third-row atoms (Kroto, 1982), e.g., sulphur ($C{=}S$, $C{=}Se$), phosphorus ($C{=}P$, $C{\equiv}P$) and Si ($C{=}Si$). At this time the so-called double bond rule—*multiple bonds involving non first-row elements should not exist*—appeared to have some validity. However, the stability of CS_2 indicated that the embargo was not total. Most importantly, as far as I was concerned, I became fascinated (while a postdoc at NRC in Canada) by the molecule $HC{\equiv}P$ which Gier had made (Gier, 1961). I became convinced that the existence of this molecule [which incidentally was produced spontaneously by a carbon arc in phosphine (!)] implied the existence of derivatives such as $ClC{\equiv}P$ and $CH_3C{\equiv}P$. I also wondered whether these species could be used as synthons to create organic phosphorus cycloaddition products (analogues of the nitrogen heterocyclic compounds) as well as metal complexes which parallel those of the metal-nitrile complexes.

The first new molecules that we created possessed carbon-to-sulphur double bonds (Kroto, 1982). Numerous compounds such as $CH_3CH{=}S$ (thioacetaldehyde), $CH_2{=}C{=}S$ (thioketene) and $CH_2{=}CH{-}CH{=}S$ (thioacrolein) were produced (with Barry Landsberg, Krini Georgiou and Rober Suffolk). They were created by thermolysis of custom-synthesised precursors and analysed by both microwave and photoelectron spectroscopy. After the success with sulphur, it seemed that the same techniques might also work for phosphorus and encouraged by Gier's $HC{\equiv}P$ result of some dozen years previously, we tried it—and it worked like a dream (Kroto, 1982)!

With my Sussex colleague John Nixon, together with Nigel Simmons and Nick Westwood, Osamu Ohashi, Keichi Ohno and James Burkett St. Laurent, we produced a whole range of these species. With Colin Kirby and Terry Cooper we also produced some elegant boron-sulphur $XB{=}S$ analogues (Kroto 1982). $CH_2{=}PH$ was my favourite as it was the first (and simplest) molecule with a carbon phosphorus double bond. Our first paper, on $CH_2{=}PH$, $CH_2{=}PCl$ and $CF_2{=}PH$ (Hopkinson *et al.*, 1976a) and the paper by Becker (1976), also on the creation of $C{=}P$ containing species, appeared almost simultaneously. Our successful creation of $CH_3C{\equiv}P$ (Hopkinson *et al.*, 1976b) was almost equally exciting as it was the first analogue of $HC{\equiv}P$. It still seems amazing that Gier's 1961 result had not been recognised sooner by anyone else as a clear sign that a whole new class of compounds was just waiting to be discovered. The creation and structural determination of species such as $CH_2{=}PH$ and $CH_2{=}PCl$ (Fig. 4), as well as $CH_3C{\equiv}P$ and other related species, were (for me) some of our most exciting advances (Kroto, 1982). Since these papers were published these compounds, which we call phosphaethenes and phosphaethynes, have become the basis of some most fruitful fields of new chemistry. However, we never got to grips with the carbon-silicon double bond—a problem solved by others—as our interests led in other directions.

During this time (ca. 1970) my colleague David Walton was perfecting techniques for synthesising very long linear chains of carbon atoms (Eastmond and Walton, 1968; Eastmond *et al.*, 1972; Johnson and Walton, 1972). These molecules appeared like perfect test-beds for quantum-mechanical study of the dynamics of bending and rotation in simple linear systems. In 1972, as luck would have it, David and I proposed a project for the Chemistry by Thesis (CT) course at Sussex, which aimed at probing such structural and dynamic behavior of moderately long carbon chains. The CT course had been

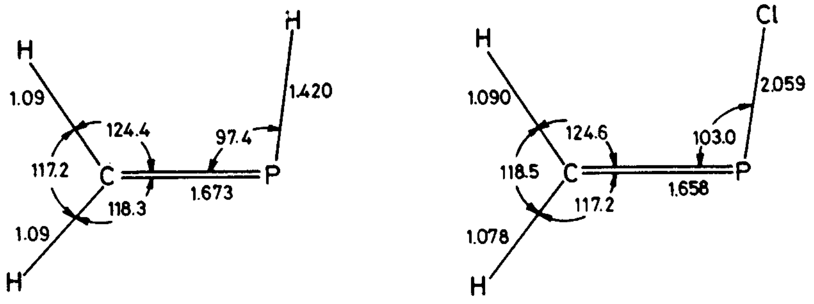


FIG. 4. The structures of the first phosphaalkynes created $CH_2{=}PH$ and $CH_2{=}PCl$, as determined by microwave spectroscopy (Hopkinson, *et al.*, 1976b; Kroto, 1982).

initiated by Colin Eaborn (1970) as a new approach to undergraduate teaching in which a BSc. degree could be obtained on the basis of a thesis which the student would write on a research topic carried out under the supervision of two tutors from different chemistry disciplines e.g., synthetic chemistry and spectroscopy). The course recognised that the traditional examination approach to the assessment of a student's ability—and in particular future capability—was an artificial and often unsatisfactory guide.

The course was unique to Sussex and produced a long stream of highly accomplished graduates with remarkably few who did not do well on the course. It *was* one of the numerous outstanding success stories of Chemistry at Sussex. I highlight "*was*" because the course has now been legislated out of existence by the combined efforts of Health and Safety Executive officials, lawyers and misguided university administrators. This is an archetypal example of how a disparate mix of uncorrelated antagonists, each focused on individual goals with no perception of the true overall consequences, can achieve negative results. A similar mix of advisors and officials in the secondary education sector has all but eliminated any real chemistry from the UK school curriculum. Today, students with any real chemical facility are virtually an extinct species.

Andrew Alexander was the outstanding student catalyst of the research project which aimed at the synthesis of a range of polyynes, in particular HC_5N, and their analysis by ir, NMR and in particular microwave spectroscopy Alexander *et al.*, 1976; Kroto, 1982). In fact it was Alex's keeness in the first place that got the project going and his enthusiasm for the work, in the second place which played a key role in its success. The start of the Sussex role in the story of C_{60} is really to be found in this project. It was the epitome of basic research and in these times when the mania for applied research is rampant, it is hard to imagine one less likely to gain support. There is little doubt in my mind that, had this project not been initiated, we at Sussex would not have been involved in the discovery of C_{60}.

HC_5N was the first molecule to be studied at Sussex on the newly arrived Hewlett Packard Microwave Spectrometer in 1974. This superb instrument enabled the rotational spectra of molecules to be measured with ease (relative to the home-built instruments that existed in most microwave laboratories at the time). The machine enabled us to concentrate almost all our attention on the demanding chemistry involved in the producing of new species without worrying about how to optimise the detection parameters. There is no doubt that much of the work we did during the 1970s would have been essentially impossible without this amazing instrument.

PHASE II. A TALE OF COLD BLACK GIANT CLOUDS AND WARM RED GIANT STARS

About the same time that we were creating the long chain carbon molecules in the laboratory at Sussex, a veritable Pandora's Box of molecules had been opened up by Townes and co-workers (Cheung *et al.*, 1968), who discovered ammonia in Orion. After this discovery microwavers and radioastronomers joined forces and showed that the vast dark clouds which lie between the stars (Fig. 5) harbour scores of molecules (methanol, carbon monoxide, formaldehyde, ethanol, hydrogen cyanide, formic acid, formamide, etc.)—all the molecules the Galaxy could possibly need for a primordial pot of prebiotic soup (Kroto, 1981). Furthermore they were all identified by the detection of their microwave rotational emission spectra using radiotelescopes. Cyanoethyne (or cyanoacetylene to we older guys) HC_3N was also detected (Turner, 1971), and when we made HC_5N I began to wonder whether it might also be present in interstellar space. It seemed like a very long shot at the time because an abundance rule-of-thumb had materialised, based on a rough correlation of available empirical data, that suggested that an additional carbon atom would reduce the abundance by ca a factor of ten, and two extra atoms implied that HC_5N should be down by a factor of 100 from HC_3N and this meant that it would be undetectable. However, my view is never to assume anything is right until it has been tested experimentally because, as often as not, assumptions are wrong and even when they are not something unexpected and interesting often happens.

However, the strong bond between laboratory spectroscopy and astrophysics, which goes back at least to Newton's time and perhaps even to antiquity, was again giving birth to yet another major new field—in this case interstellar astrochemistry. Molecular radioastronomy was the crucial medium in uncovering the hordes of molecules—indeed it has now been shown that the molecules play a crucial role in the collapse of the clouds to form stars. As gravitational attraction causes the inter-

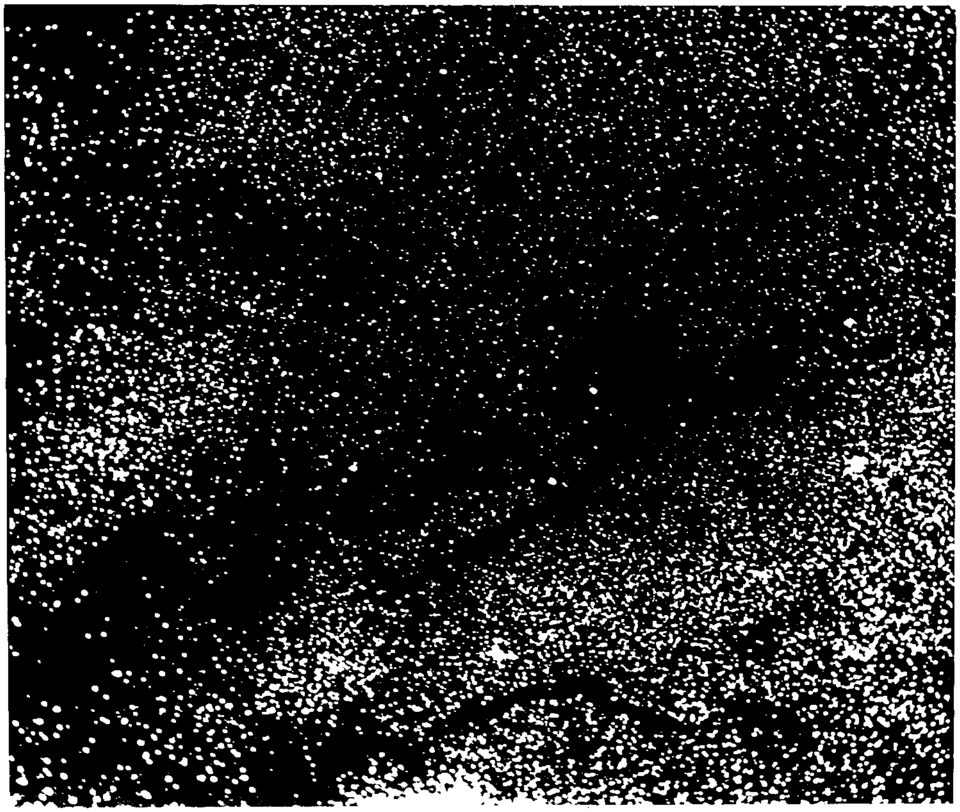


FIG. 5. The dark clouds in Taurus from Barnard's (1927) *Atlas of Selected Regions of the Milky Way* (edited by E. B. Frost and M. R. Calvert). Heile's Cloud 2 is the dark area in the lower left-hand corner.

stellar gas clouds to collapse and heat up, rotational transitions (mainly of CO) leak radio energy out, allowing further cloud collapse to occur, ultimately to such high pressures and temperatures that new stars and planets can form.

I wrote to my friend Takeshi Oka (we had both been postdoctoral fellows at NRC during the "golden years" when NRC had been the outstanding national research facility) and asked him whether he was interested in searching for HC_5N in space. He turned out to be as keen as I was. Together with NRC astronomers Lorne Avery, Norm Broten and John McLead, we detected the molecule in the giant molecular cloud SgrB2 towards the galactic centre (Avery *et al.*, 1976). The discovery was really a surprise because the molecule turned out to be much more abundant than expected—one more example of why one should never let a theoretical assumption deter one from carrying out an experiment.

The next question was clear—was HC_7N present? David Walton worked out a synthesis and Colin Kirby set about the demanding task of synthesising it and measuring the rotational frequencies (Kirby *et al.*, 1980). After making it in the laboratory and searching for it in a dark cloud in Taurus, Fig. 5, using the 46-meter radio dish in Algonquin Park, Canada we found that it, too, was present, Fig. 6; Kroto, Kirby, *et al.*, 1978; Kroto, 1981, 1986). It scarcely seemed possible. This family of molecules was making total nonsense of the abundance rule-of-thumb which almost all other families of molecules appeared to follow. Then, just as we at Sussex were about to attempt the daunting task of synthesising HC_9N, Takeshi found a clever way of estimating its rotational frequencies by extrapolation from the known frequencies of the set HC_nN ($n=1,3,5,7$) (Oka, 1978); and we detected it as well (Broten *et al.*, 1978). These were then the longest and heaviest molecules conclusively detected in space—and still remain so nearly 20 years later. From these discoveries it became clear that there was a problem: The ion-molecule reaction theories of Klemperer, Herbst, Dalgarno and Black (Herbst and Klemperer, 1973; Dalgarno and Black 1976), which accounted almost perfectly for almost all the other species observed, were just not able to account for the high abundances of such long carbon chains. It seemed to me that some alternative source was needed and fortunately a possible answer started to appear. As time progressed cool red giant carbon stars, such as the fascinating object IRC+10216 (Becklin *et al.*, 1969), were found to be pumping the chain molecules out into the interstellar medium.

PHASE III. TEN DAYS IN SEPTEMBER 1985

During the early 1980s Robert Curl visited my laboratory at Sussex and invited me to come to Rice University in Houston at some time in the future. During Easter 1984, just after attending the Conference on Molecular Structure that Jim Boggs organised biennialy in Austin, I took up the invitation and visited Rice. Apart from this superb conference another good reason for going to Texas is that there are excellent "Half-Priced Books"stores in Austin, Houston and Dallas. When I arrived in Houston, Bob was enthusing about a very recent result that Rick Smalley and his group had just obtained. They had shown that SiC_2 was a triangular molecule (Michalopoulos *et al.*, 1984)—a fascinating result. The way in which the Si had avoided forming a classical double bond in this species, at a stroke, explained why we had had so much difficulty observing molecules with Si═C bonds. It also fitted in nicely with the flexibility of C_3 and OC_3O which I had studied years before. I went over to Rick's laboratory, where he enthusiastically described how his cluster beam machine worked. He explained how a pulsed laser, focussed on a metal disc, vaporised material, producing atoms which were swept up by pulses of helium which caused clustering and concomitant cooling. Then, by expansion through a nozzle into a vacuum, they are cooled further, and by skimming into a pulsed beam which is analysed by a time-of-flight mass spectrometer one can ascertain the cluster mass distributions. As Rick described the mode of operation, it reminded me of previous work on carbon clusters, particularly by Hintenberger and coworkers (1963), and I began to wonder whether, by substituting a graphite target disc for the metal one, the plasma produced by the laser might simulate the circumstellar shell of the cool red giant carbon stars such as IRC+10216 and produce the carbon chains. This would give strong support for the stellar solution to the chain problem and provide an important alternative mechanism to the ion-molecule schemes.

As that day wore on, I thought more and more about the idea and became more and more convinced that Rick's apparatus was the key to proving a circumstellar source of the chains. Furthermore the detection of the spectrum of SiC_2 suggested that the apparatus might be able to confirm the conjecture of Alex Douglas (1977) that the carbon chains might be carriers of the Diffuse interstellar Bands (DIBs) (Herbig, 1975). The DIBs are interstellar spectroscopic features which have puzzled astronomers and spectroscopists since the 1930s. That night I described these ideas to Bob who was keen to collaborate—particularly on the second much more difficult DIB problem. In the event, in August 1985, Bob called me at my home in the UK to say that my experiments were to be carried out at Rice imminently and asked whether I was interested in coming to Houston. I didn't need to be asked twice—I dropped everything and within three days I was in Houston.

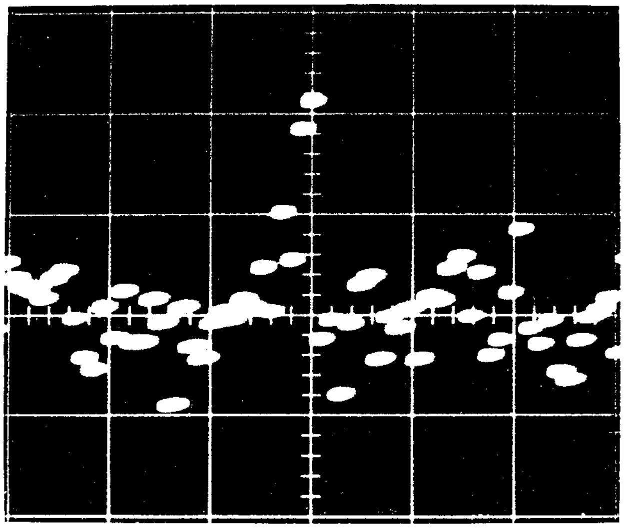


FIG. 6. A photograph of the first oscilloscope trace of the radio signal due to interstellar HC_7N in Heiles's Cloud 2 in the constellation of Taurus (Fig. 5).

As soon as I arrived I gave a concentrated 2–3-hour seminar on all aspects of interstellar molecules and their spectra. I met Jim Heath, Yuan Liu and Sean O'Brien, the key students with whom I was to work intimately for the amazing ten-day period from 1st to 10th September 1985. Jim Heath and I struck an instant rapport partly because we are both addicted to books and enjoy browsing in bookstores. So after long stints on the apparatus (Ap2 as Rick affectionately called his second-generation cluster beam machine) Jim and I would occasionally play hooky to visit Houston bookstores. We would invariably end up, often accompanied by Carmen (Jim's wife) and Sean, late in the night at the House of Pies, a Houston 24-hour coffee bar which served outstanding

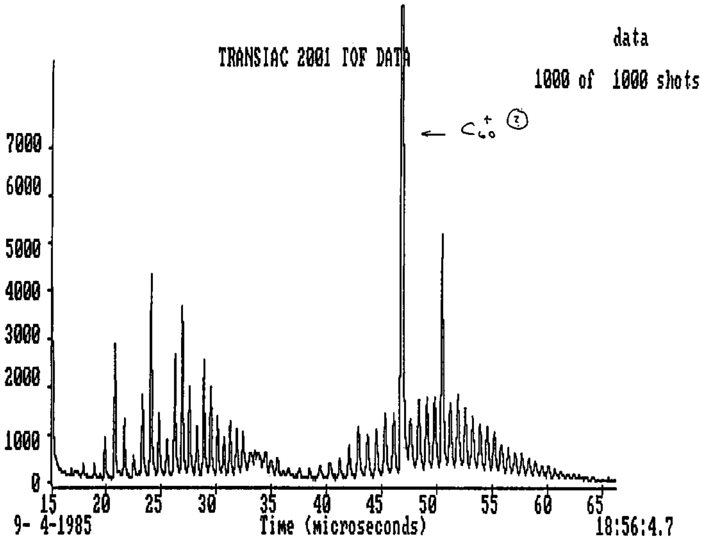
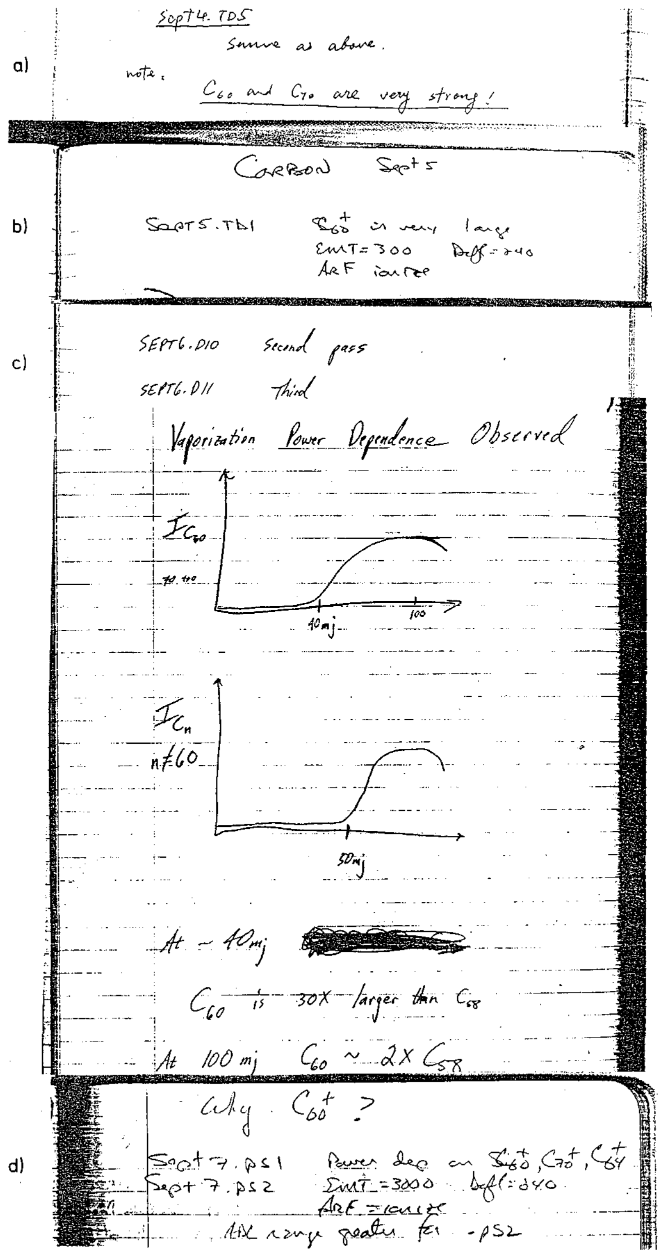


FIG. 7. Annotated time-of-flight mass spectrum of carbon clusters produced on Wednesday 4th September 1985, the day on which the dominance of the C_{60} signal was first recorded [see Fig. 8(a)].


a)

Sept4. TD5

Same as above.

note. C_{60} and C_{70} are very strong!

b)

CARBON Sept 5

SEPT5.TD1 C_{60}^{+} is very large

EMT = 300 Defl = 240

ArF source

c)

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}

d)

Why C_{60}^{+}?

Sept 7.PS1 Power dep on C_{60}^{+}, C_{70}^{+}, C_{64}^{+}

Sept 7.PS2 EMT = 3000 Defl: 240

ArF = source

Att range greater for .PS2

FIG. 8. Entries in the Rice Cluster Laboratory Notebook from the period 4th–7th September, 1985, when key experiments were carried out at Rice University. (a) Sept. 4th; (b) Sept. 5th; (c) Sept. 6th; (d) Sept. 7th. Entries by Heath, Liu and O'Brien.

Dutch apple pie. Apparently (according to a recent TV programme on the history of the PC) the founders of COMPAQ hatched their company at the House of Pies.

The experiments began on September 1st, and the good news is that they were successful. Almost immediately we detected the linear molecules with 5 to 9 carbon atoms that we had observed in space (Kroto, Heath, *et al.*, 1987) and thus we got the evidence needed for the idea that the chains could easily have originated in red giant stars. The bad news is that an interloper was present. As the results emerged, our attention was quickly attracted by the precocious antics of this uninvited guest. It had 60 carbon atoms and was accompanied by a more diminutive but still fairly prominent partner with 70 carbon atoms. These characters actually had already appeared in a publication some twelve months previously by Rohlfing, Cox and Kaldor (1984), and another group, Bloomfield *et al.* (1985) had also been probing their properties. I had actually read the Exxon paper in some detail at the time it appeared because it described almost exactly the experiments I had proposed to the Rice group a few months previously. I had not however been moved to rub 60 brain cells together to divine what might be going on and apparently neither had anyone else. The Exxon group had made the discovery that a new family of carbon clusters with more than 30 atoms existed which appeared only to be even numbered. Though C_{60} was definitely more prominent than its neighbours, it was not sufficiently prominent to attract any particular attention, and was certainly not dominant as it was after Jim and Sean had finally finished with it.

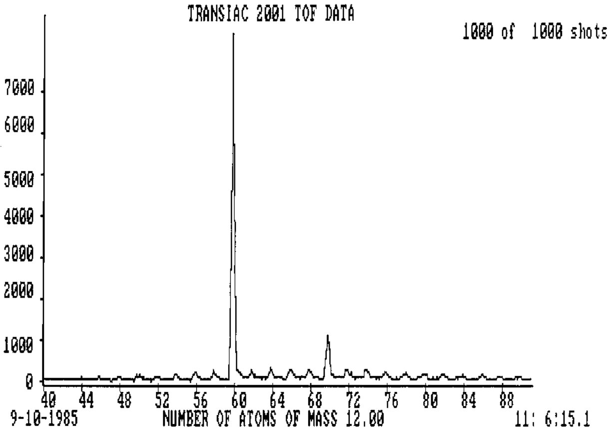


FIG. 9. Time-of-flight mass spectrum of carbon clusters under the optimum conditions for the observation of a dominant C_{60} signal obtained by Jim Heath on Monday 9th September 1985.

The strongest peak in the 30–100 atomic mass range of the mass spectrum was usually the peak for C_{60} and it was used to tee up the experimental parameters for these larger species. During these studies, conditions were discovered which gave a distribution in which C_{60} was completely off scale (Fig. 6). This observation was made on Wednesday September 4th and our reactions were written up in the lab notebook by the graduate students (Fig. 7). Two days later, on Friday, a group meeting took place at which Jim and Sean offered to work over the weekend to optimise conditions. Sean worked that evening and Jim took over the next day and worked all weekend on the problem of optimizing the signal (Fig. 8). By Sunday evening (8th September) the result was the spectrum shown in Fig. 9, which exhibited almost nothing but the C_{60}, with C_{70} as a somewhat smaller but still prominent chaperone.

As C_{60} and its sidekick became the prime focus of our attentions, I began to call these peculiar *wadges* of carbon the Lone Ranger and Tonto or sometimes Don Quixote and Sancho Panza. Our deliberations came to a climax during discussions on Monday the 9th. C_{60} ap-

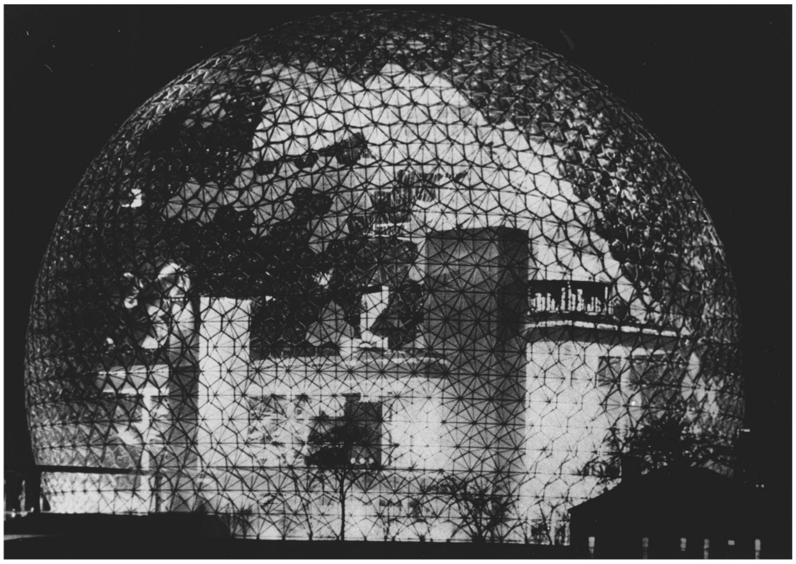


FIG. 10. Photograph taken by Michel Proulx of the Geodesic Dome designed by Buckminster Fuller for the US exhibit at Montreal EXPO67 (Proulx, 1967). One of the pentagons necessary for closure is discernible in this photograph. The variation in the strut lengths of the hexagons in the vicinity of the one pentagon visible, necessary to achieve a relatively smooth round surface, can also be discerned.

peared to be really quite unreactive, a behaviour difficult to reconcile with a flat hexagonal graphene sheet—the most obvious first thought that would occur to anyone—which must have some 20 or more dangling bonds. After all, the chains had ends (two) and they added on two H atoms; thus a 60-atom flat hexagonal graphene sheet should add on ca. 20 or more H atoms, but it did not. As we sought a solution, we discussed many possible structures that might explain the perplexing results.

Gradually a consensus developed that what might have happened was that flat hexagonal sheets had either formed or ablated from the surface of the graphite disc and closed into a cage, so eliminating the reactive edge. The closed hexagonal cage idea reminded me of a visit with my family to Expo67 in Montreal, where Buckminster Fuller's dome had dominated the horizon. It particularly called to mind an image of the dome in an issue of *Graphis* magazine (Proulx, 1967) devoted to the exhibition (Fig. 10). Rick went to the Rice Library and extracted a book about Buckminster Fuller and his inventions (Marx, 1960). I also recalled a"stardome" skymap, Fig. 11(a), which I had built for my children some years before. I remembered that the stardome had not only hexagons but also pentagons and wondered, as Bob and I went home for lunch, whether I should call my wife at home back in England to check whether or not it had 60 vertices. As I was scheduled to leave for the UK the next day, I invited the team out for dinner at a Mexican Restaurant to celebrate the exciting discovery. Needless to say we spent all the time at the restaurant trying to solve the puzzle.

That evening/night Rick experimented with sheets of hexagons, Jim together with Carmen experimented with toothpicks and jelly beans, and Bob and I discussed the stardome solution again. Rick could not make any progress until he remembered our discussion of the pentagons in the stardome (Smalley, 1991). Rick discovered that the structure started to curve into a saucer shape as soon as pentagons were included among the hexagons and finally closed as he added a twelfth pentagon. The next morning, when he revealed his paper model, Fig. 11(b), I remember being ecstatic. It was beautiful and looked just like the stardome, Fig. 11(a), as I remembered it. It is of course a truncated icosahedron, and the fact that it turned out to be a football too was most appropriate. After all, the whole discovery story is an archetypal example of team effort. I remember thinking that the molecule was so beautiful that it just had to be right—and anyway even if it were not, everybody would surely love it, which they did—eventually! My suggestion that we call the molecule Buckminsterfullerene (the -ene ending fitted perfectly) was, after some discussion, accepted and we sent off the paper to *Nature*—the date of receipt was 13th September (N.B. the experiments had started on 1st September).

PHASE IV. LITTLE FULLERENES, GIANT FULLERENES, RED SOLUTIONS, AND ONE-LINE SOLUTIONS, OR, HOW TO PLAY FOOTBALL WITHOUT KNOWING THE RULES

We decided to probe the consequences of the C_{60} discovery, and experiments were initiated at Rice (Heath *et al.*, 1987). Jim Heath, Sean O'Brien, Yuan Liu and Qing Ling Zhang were among the most heavily involved students. A series of experiments was also initiated at Sussex: with Tony Stace, a cluster beam machine was constructed by a highly dedicated set of students (Simon Balm, Richard Hallett and Wahab Allaf) and we thus started to probe cluster behaviour in general. With the aid of support from British Gas (via Steve Wood) we also started to probe the implications of our discovery for combustion.

One of the most charismatic things about C_{60} and one which continually lay simmering in the back of my mind, was the fact that all the carbon atoms in C_{60} are equivalent, and so the ^{13}C NMR spectrum should consist of but a single elegant line. However, how could one make enough to measure it? That was a daunting task and I must admit that whenever my thoughts drifted onto this subject they invariably ended with the conclusion that

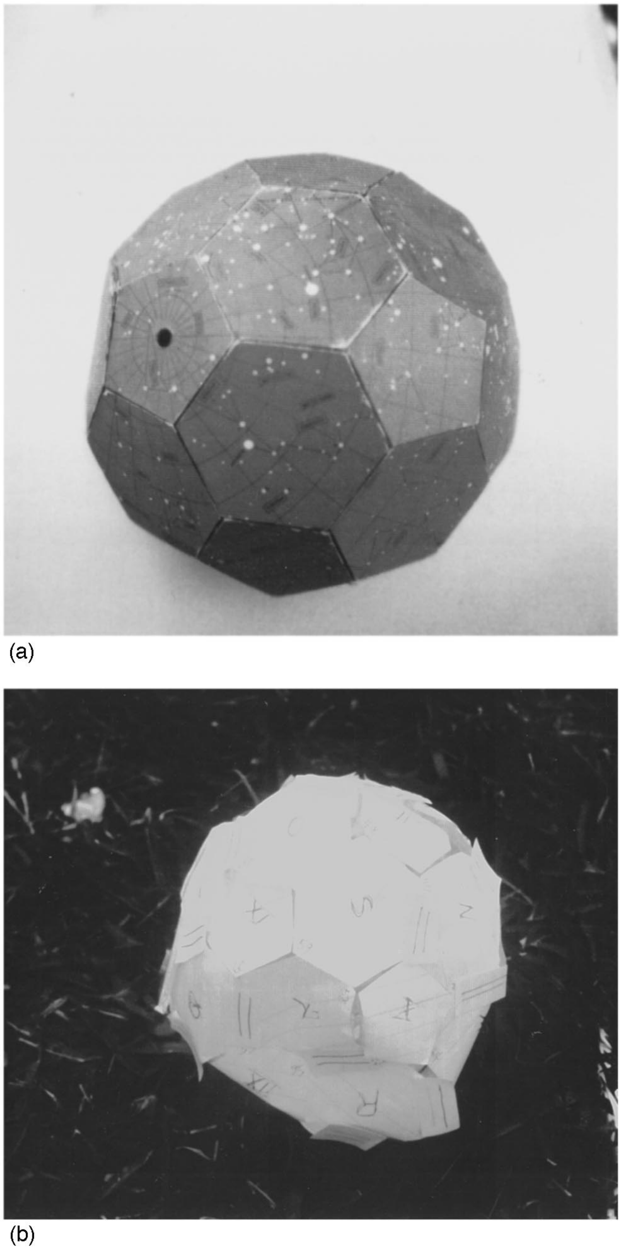


FIG. 11. The two card models which played key roles in the positing of the truncated icosahedral structure of C_{60}. (a) top Stardome map of the sky (Buckminster Fuller patented *t*-icosahedral and other polyhedral world map projections); (b) bottom protoype C_{60} made by Smalley. Both models are truncated icosahedra with 60 vertices, 12 pentagonal and 20 hexagonal faces.

one day some young, ingenious, upstart, synthetic organic chemist would surely observe it first. I certainly never entertained much hope of observing the line at Sussex and so it was not really an objective. It is important to understand how impossible such a task appeared at that time. My attitude to the research was to probe those aspects of the C_{60} discovery which particularly puzzled me and let the research flow whichever way it would.

A few days after the discovery I arrived back in Europe and announced our discovery and our conjectured structure at a conference in Riccione. Julie August, a former student now working at Nottingham, told Martyn Poliakoff of the discovery and he sent me a zerox copy of the idea that David Jones had had in 1966 (Jones, 1966,1982). Writing under the pseudonym of Daedalus in the Ariadne column of the *New Scientist*, David had proposed the amazingly imaginative idea that large carbon balloons might be feasible. We also discovered that C_{60} itself had already been proposed by Osawa in a Japanese article 15 years earlier (Osawa, 1970) and in a book with Yoshida (Yoshida and Osawa, 1971). Not only that, Bochvar and Gal'pern (1973) had even carried out a Huckel calculation and published the pattern of the molecular orbitals (Stankevich *et al.*, 1984). We also discovered that Orville Chapman at UCLA had initiated a programme aimed at the synthesis of the molecule (private communication). In retrospect it is rather peculiar that this charismatic molecule had not attracted the attention of the chemistry community earlier. Jones, in his articles (1966,1982) introduced me to D'arcy Thompson's book *On Growth and Form* (Thompson, 1942) and pointed out that Euler's Law indicated that no sheet of hexagons could close. If, however, 12 pentagons were introduced into a hexagonal sheet of any size it would close. Almost everybody (who knows any organic chemistry!) knows that unsaturated molecules with adjacent pentagonal rings are extremely unstable. Thus from Jones' article it became immediately obvious that as $5\times12=60$, C_{60} had to be the smallest cage able to close *without* abutting pentagons. Thus the secret of C_{60}'s stability was beautifully simple. It lay in the accommodation of the two requirements: Euler's 12-pentagon closure principle and the chemical stability conferred by pentagon nonadjacency. I consider these two points to be the "2+2" of Fullerene stability. Schmalz, Seitz, Klein and Hite, using circuit theory, placed these principles on a firm theoretical basis (Schmalz *et al.*, 1986). The C_{70} peak was, as mentioned previously, also prominent and Rick found an elegant and a plausible structure, in which two C_{30} hemispherical halves were separated by a ring of ten extra C atoms. This was proposed in the paper describing the crucially important discovery, which Jim Heath made, that atoms (such as La could be put inside the cage (Heath *et al.*, 1985). This discovery (and its refinements), that endohedral complexes could form, was perhaps the strongest empirical observation supporting the cage proposal prior to extraction in 1990.

During some moments of musing over these two stability criteria I began to wonder about the identity of the next cage (after C_{60}) which might be able to close without abutting pentagons. I started to play around with a model of C_{60} by adding atoms and before I had made much headway it suddenly struck me that perhaps closure could not occur again until C_{70} (Fig. 12). If that were the case it would explain—at a stroke—the prominence of C_{70}. That seemed to me a most unexpected and certainly not very obvious result. Furthermore a subtle circular argument appeared—if it were true, then closure demanded that C_{70} be strong and that would be, for me, by far the most convincing support for the fullerene

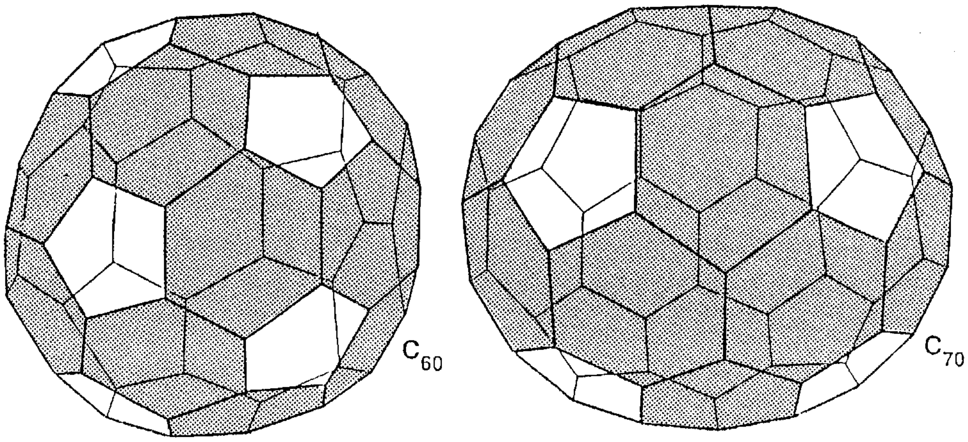


FIG. 12. For species with fewer than 72 atoms these two structures are the *only* ones which can be constructed without abutting pentagons. Thus, on the basis of the *pentagon isolation principle* (Kroto, 1987; Schmalz *et al.*, 1988) and geodesic considerations, C_{60} and C_{70} are predicted to be the first and second fullerene magic numbers, respectively. This result provided the simplest and most convincing circumstantial evidence in support of the closed cage concept prior to extraction.

proposal and I knew that there was not a hope in hell of an alternative explanation of *both* the 60 *and* 70 magic numbers. I knew from that moment on that one day we would be proven right.

A call to the Galveston group to see whether they could prove the conjecture was in order. To my absolute delight Tom Schmalz told me that they had already shown that cages with 62, 64 and 66 atoms could not close without abutting pentagons and that the analysis on 68 atom cages was in mid-stream at that very moment. Thus the *Pentagon Isolation Rule*, which governs general fullerene stability, was born (Kroto, 1987; Schmalz *et al.*, 1988). Another thought struck me during the phonecall with Schmalz. I remembered that C_{50} was often a magic number in some of our experiments and suggested that they might check whether the 50-atom cage might be the smallest cage to close without *triplets* of abutting pentagons. Schmalz *et al.* showed this to be the case too (Schmalz *et al.*, 1988). I wondered about a result that Sean had obtained (O'Brien *et al.*, 1988). He had found that laser irradiation of C_{60} caused it to fragment by reducing the size of the clusters more or less sequentially by even numbers from 60 to 58 to 56 etc. . . . all the way down to 32. After 32 further irradiation blew the cluster into small fragments. I tried to push the pentagon multiplet isolation idea to quartets in the hope that it would explain the C_{32} result, but to my amazement and delight an elegant C_{28} (Kroto, 1987) formed in my hands (Fig. 13). This reminded me of a result that had puzzled us for some time—in some of our runs the 28 carbon atom signal sometimes rivalled that of C_{60}. It also struck me that this species should be a sort of superatom cluster analogue of the carbon atom itself with effective tetravalency suggesting that an elegant tetrahedral $C_{28}H_4$ derivative (Fig. 13) might actually be a stable molecule (Kroto, 1987). Indeed, in some Exxon data (Cox *et al.*, 1988), I found just the mass spectrum distribution which confirmed that the isolation principle could be generalised to include various sizes of multiplets and account for magic numbers of smaller cages down to C_{20} (Kroto, 1987, 1988). It not only exhibited magic numbers at 60, 50 and 28 but it stopped abruptly at 24. From Patrick Fowler I had learned that no cage could be constructed with 22 atoms (Fowler and Steer, 1987). Thus there appeared to be "semistable" fullerenes (at least in beams) down to C_{20} which were predictable (Fig. 14) on the basis of the cage closure concept. What more "proof" could one possibly want for the whole fullerene concept? None.

Then one day I decided that we should build our own Buckminster Fuller domes, or rather molecular models of the giant fullerenes (Kroto, 1990) and ordered 10 000 carbon atoms (molecular model atoms and bonds). Ken McKay, armed with Goldberg's (1937) paper and Coxeter's (1963) book, set about building C_{240}, C_{540} and later C_{960} and C_{1500} with icosahedral symmetry. When Ken came in with the model of C_{540} it was beautiful, but I could not quite understand its shape—the model was not round like Buckminster Fuller's Montreal dome but had clear icosahedral tendencies (Fig. 15) (Zhang *et al.*, 1986). Indeed, Ken's model had cusps focused at the 12 pentagons and from a distance had a definite polygonal outline. Then we realised that the structure explained some very interesting results that Sumio Iijima had obtained (Iijima, 1980). He had observed concentric-shell

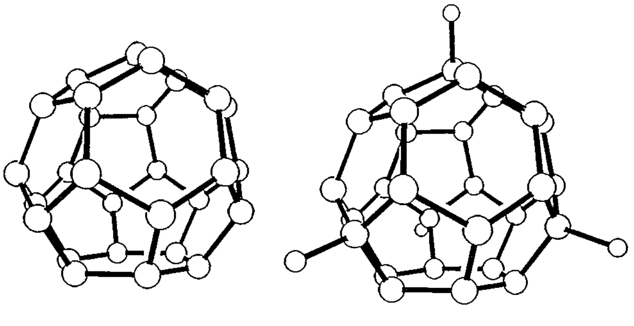


FIG. 13. The tetrahedral small fullerene C_{28} (left) and the tetrahydrogenated derivative, $C_{28}H_4$ (right), which is expected to exhibit some stability (Kroto, 1987).

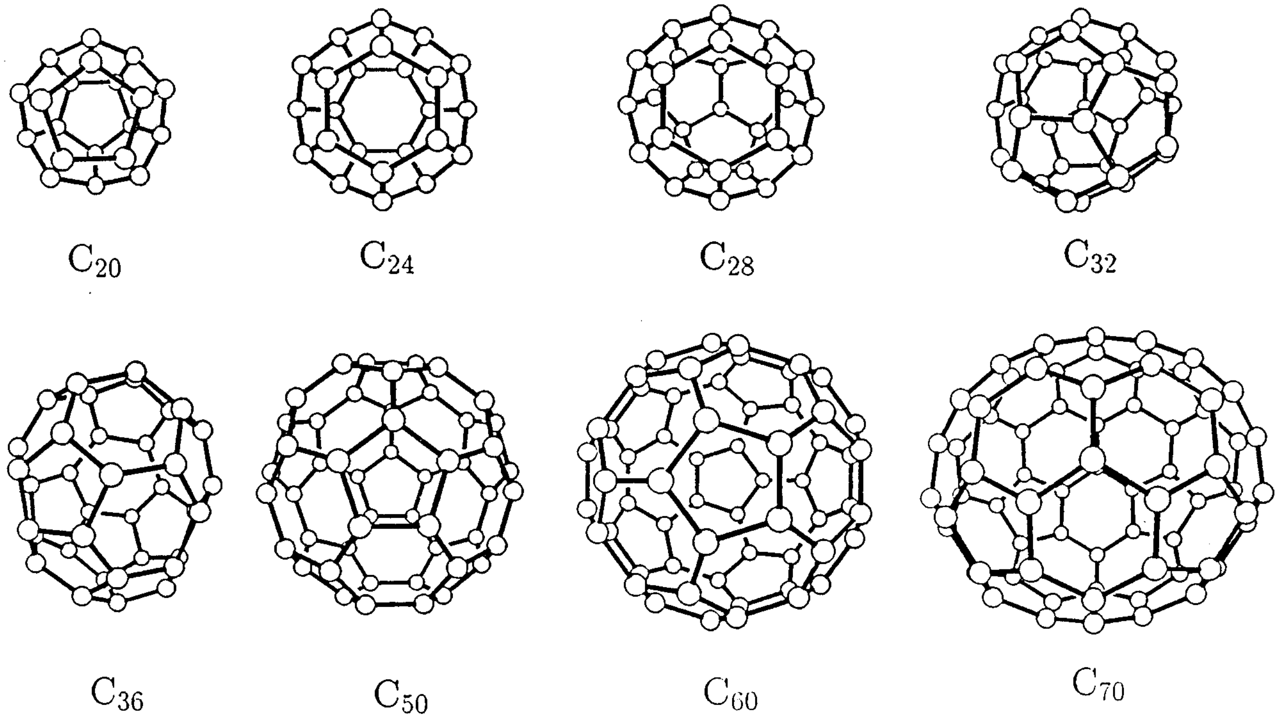


FIG. 14. A set of fullerenes between C_{20-70} some of which are magic and others of which are predicted to be "semi"-magic (Kroto, 1987; Schmalz *et al.*, 1988).

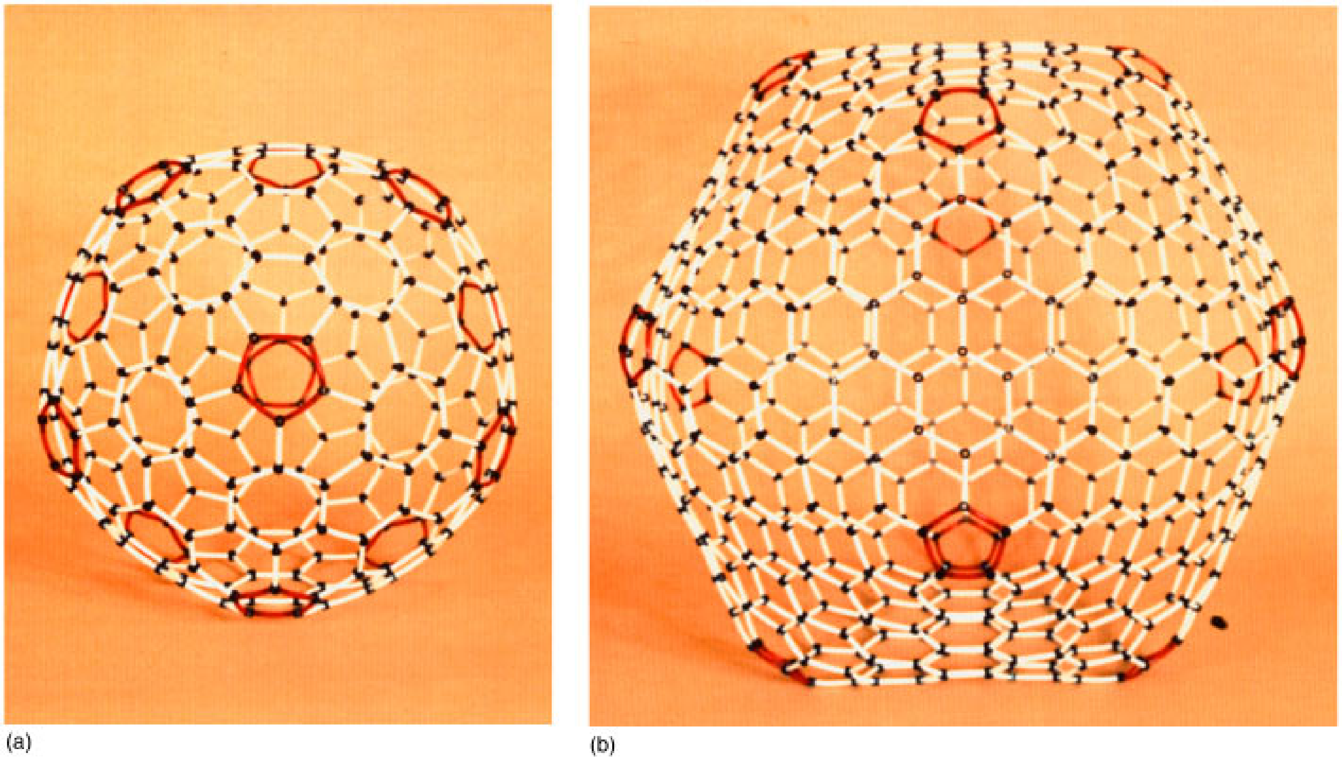


FIG. 15. (color) Photographs of molecular models of the giant fullerenes C_{240} (left) and C_{540} (right). The models turned out to possess icosahedral shapes rather than perfectly spheroidal ones similar to the geodesic domes. Each of these structures can be considered as an initially flat hexagonal network which has warped into a closed monosurface (of icosahedral symmetry) by 12 pentagonal disclinations which give rise to the cusps. These structures provided the first prediction of faceting in closed cage carbon species such as giant fullerenes and nanotubes.

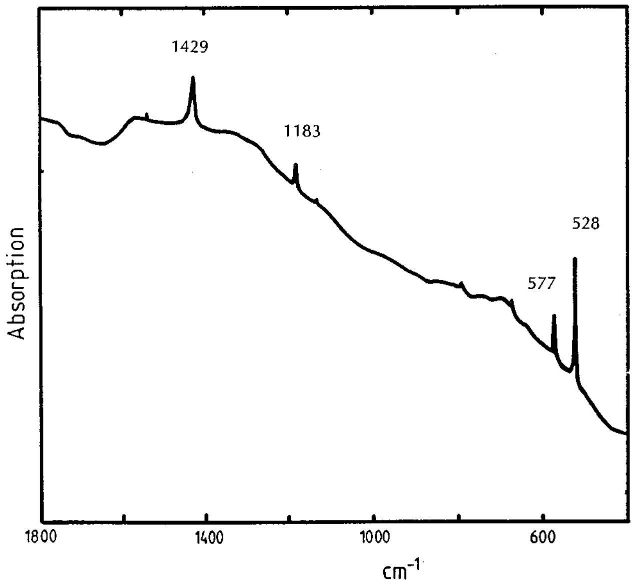


FIG. 16. The four historic IR bands observed by Krätschmer, Lamb, Fostiropoulos and Huffman, from Krätschmer, Fostiropoulos, and Huffman, 1990b.

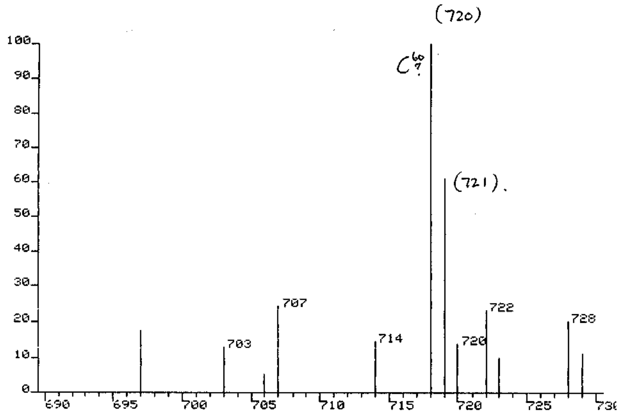


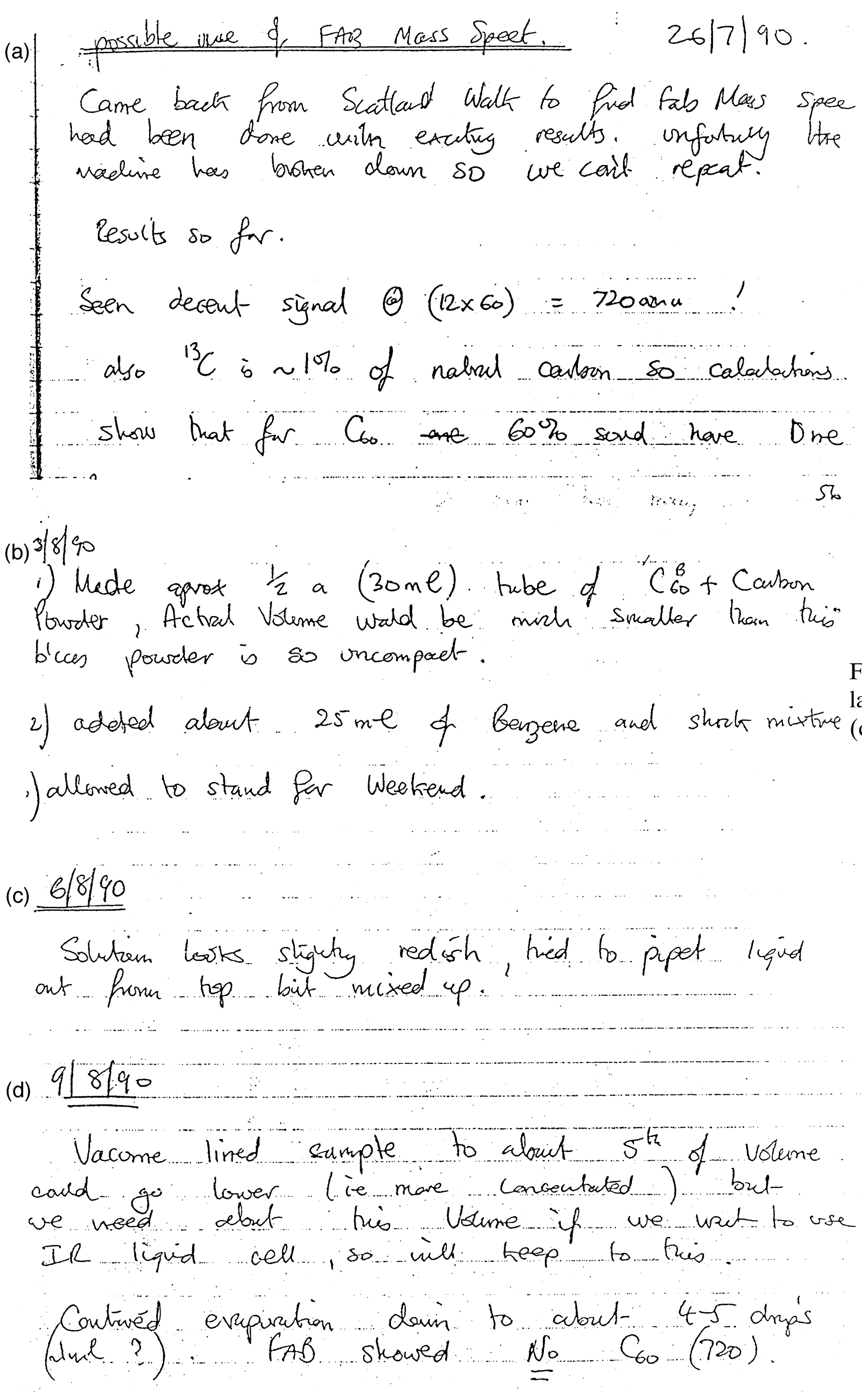
FIG. 17. Fast atom bombardment (FAB) mass spectrum of a deposit of arc-processed soot obtained on 23rd July 1990 at Sussex by Ala'a Abdul-Sada. The machine calibration is out by 2 amu, but the isotope pattern was convincing as the peaks are close to the intensity ratio 1.0:0.66:0.22, as expected for $^{12}C_{60}$: $^{12}C_{59}{}^{13}C$: $^{12}C_{58}{}^{13}C_2$.

onion-like carbon particles by transmission electron microscopy. Superficially many of Iijima's particles appeared to be round, as one might assume if they were nanoscale geodesic domes. However, because of this assumption I had glossed over some crucial subtle features in the micrographs—the outlines were not quite as round as they superficially appeared. The outlines were actually polygonal (Kroto and McKay, 1988; Kroto, 1988). In fact, as we looked more carefully at the infrastructure of Buckminster Fuller's domes we realised that the strut lengths in the vicinity of the pentagons had been adjusted to give them a smooth spheroidal shape (Fig. 10). Thus the C_{60} discovery had led to an elegant explanation of a previously unexplained result. It showed that a cage with an icosahedral shape could be constructed *entirely* from sp^2 carbon atoms. Thus 12 pentagonal disclinations—a minimal number of defects by comparison with those found in any normal crystals—would convert a perfectly flat graphene sheet of any size into a closed cage.

There is a rather nice lesson to be drawn from this advance: There had been no premeditated research aim—the original reason for constructing the giant fullerene model was solely for the intrinsic interest and pleasure of building an elegant structure—and yet it revealed an unexpected result. The result had important consequences. For instance, it was the first study of the way that the inclusion of pentagons influences the curvature of a graphene sheet—a result that was to find particular use later when elongated giant fullerenes (nanotubes) were discovered. On occasion I would wonder about our cage proposal, reassess each and every observation: 60 and 70 should be magic numbers; 50, 28 were also explainable magic numbers; there was no clear evidence of C_{22}; the icosahedral shape of the giant fullerenes could be explained; Jim had observed metal complexes that behaved as though they were endohedral (Heath *et al.*, 1985); Sean had found that C_2 units were ejected (O'Brien *et al.*, 1988) and there were other supporting experimental results (Curl and Smalley, 1988; Smalley, 1991). It all fitted perfectly, there was no way we could be wrong.

I thought we should probe the Iijima result and see whether C_{60} might reveal some clues about the round particles in general. This was based on the idea we had proposed (Zhang *et al.*, 1986) that the mechanism of C_{60} production might be related to soot formation. We were able to acquire an old carbon arc evaporating unit and drill a hole in the base plate to admit He. Ken McKay monitored the structure of the carbon deposit by scanning electron microscopy as a function of He pressure. The idea was that as the He pressure increased C_{60} formation might be initiated, and this would be accompanied by the creation of round carbon particles. A change in the deposit did occur as the pressure rose above 50 microns (Kroto, 1992a). The next step *seemed* obvious—to monitor the possible production of C_{60}. However, I made a fatal error. I assumed that if C_{60} were created in the arc, it would only be in minuscule quantities and only the most sensitive of detection techniques available (mass spectrometry) would work. I then tried, for the next two years (unsuccessfully), to obtain the financial support for a quadrupole mass spectrometer.

I was still trying, with Geoff Cloke, to get a mass spectrometer when we learned of a study by Krätschmer, Fostiropoulos and Huffman, who had detected four infrared hands [Fig. 16—exactly as predicted theoretically (Disch and Schulman, 1986); Newton and Stanton, 1986; Wu *et al.*, 1987) in a carbon deposit made in exactly the same way as ours (Krätschmer *et al.*, 1990b)]. If this were correct then their deposit (and ours also!!!) must contain at least 1% C_{60}. I could not believe it—and yet there were four sharp resonant frequencies in the pure carbon deposit. What on earth could they be? I decided



(a) 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) = 720 amu !

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

56

(b) 3/8/90

i) 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

) allowed to stand for Weekend.

(c) 6/8/90

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

(d) 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 (dud ?). FAB showed No C_{60} (720).

FIG. 18. Entries by Jonathan Hare in his laboratory notebook (a) 26/7/90; (b) 3/8/90; (c) 6/8/90; (d) 9/8/90.

to check out this incredible (in its literal meaning) result and proposed it as a third-year project for Amit Sarkar (an undergraduate) to work on with Jonathan Hare (graduate student) to see whether they could repeat it—and they did!!! (Kroto, 1992a). It is difficult, today, to explain just how difficult it was to accept the Krätschmer *et al.* observations, but it is important, for an understanding of how science advances, to try. How could C_{60} have remained undetected until the end of the 20th century if it could be produced in such a yield by this seemingly simple approach?

We then tried to see whether the deposit gave a mass spectrum and Ala'a Abdul Sada obtained a 720 mass signal [Figs. 17 and 18(a)]—it still seemed impossible. I was still very suspicious, especially as I knew that C_{60} can be formed readily during the mass spectrometric sampling process. The mass spectrometer then broke down [Fig. 18(a)]. Over the years we had often discussed the likely physical properties of C_{60}. Some thought it would be a high-melting-point solid, others thought it would be a liquid or even a gas. On a Friday evening 3rd August Jonathan decided, with the unblinkered optimism that only the young possess, to test whether the species would dissolve in benzene [Fig. 18(b)] and amazingly produced a red solution which he placed on my desk on Monday morning (6th) [Figs. 19 and 18(c)].

FIG. 19. (color) Original reddish extract obtained by Jonathan Hare on Monday 6th September 1990.

Jonathan seemed to have no difficulty in accepting that it was C_{60} as is indicated by the fact that he called it $C_{60}{}^{B}$ (Fig. 18) which was our shorthand notation for Buckminsterfullerene. On the Thursday some of the solution was concentrated to see whether a deposit could be obtained which would yield a stronger 720 mass spectrum—but it didn't [Fig. 18(d)]. This was exactly the right experiment and actually a rather difficult one for technical reasons and would almost certainly have worked the next time—had there been one(!).

The next day, disaster struck—I had a call from *Nature*; Philip Ball asked whether I would referee a new paper by Krätschmer *et al.* When the manuscript arrived by fax at around 12 noon it was a bombshell. Krätschmer *et al.* had also obtained a red (!!!!) solution and what is more their solution had yielded crystals (Fig. 20) which x-ray analysis conclusively indicated consisted of arrays of spheroidal molecules exactly the right size to be C_{60}. There was absolutely no doubt about it—Wolfgang Krätschmer, Lowell Lamb, Kostas Fostiropoulos and Don Huffman had done it (Krätschmer *et al.*, 1990). It was only at that moment that I suddenly realised that we had been in a race, and we had been pipped at the post. I considered committing suicide, but decided to go for lunch instead. Over lunch I read and re-read this fantastic manuscript and I doubt whether I shall ever have an experience like it again. It was a very strange mix of alternating feelings: First, exhilaration from being proven right, and then disappointment from having come so close to proving it ourselves. After lunch I called back Philip Ball and told him to accept the paper immediately.

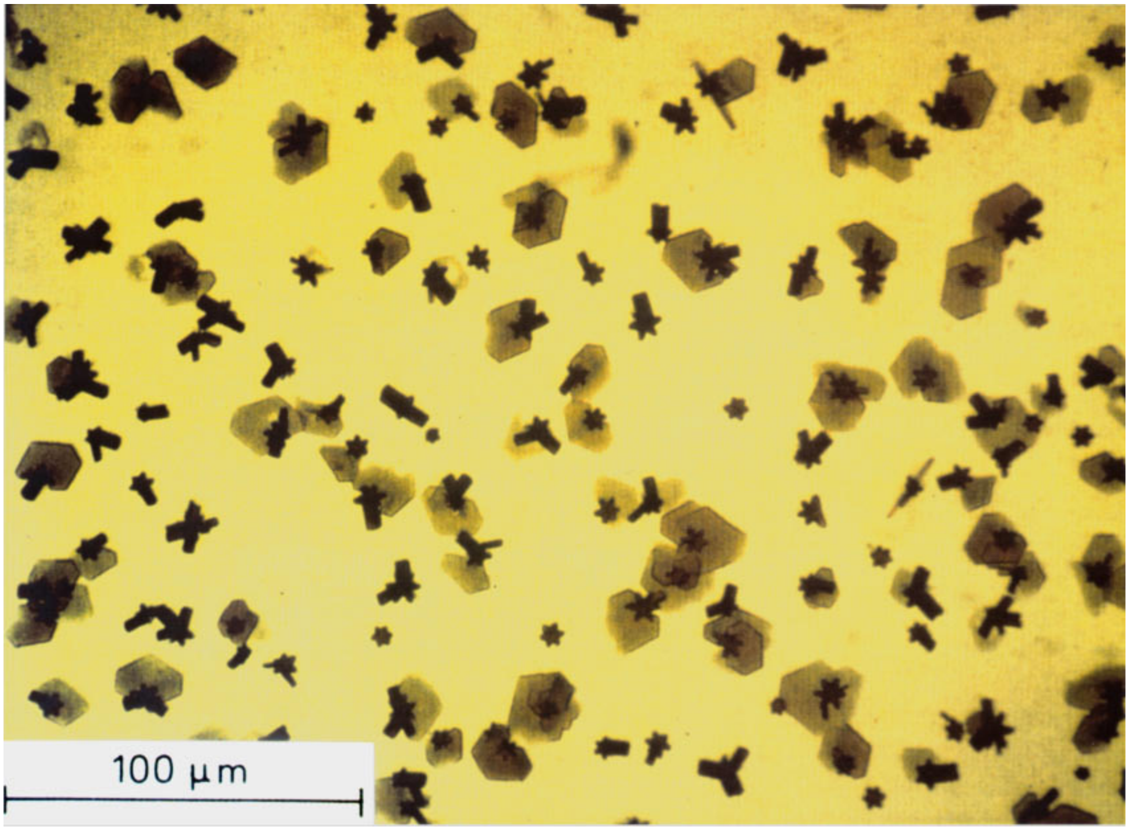


FIG. 20. (color) The astounding photograph of crystals of pure carbon which Krätschmer, Lamb, Fostiropoulos and Huffman obtained during their breakthrough in extraction; Krätschmer, Lamb, Fostiropoulos, and Hoffman, 1990.

But what to do now? It was difficult to think at all, let alone make any sensible decisions. However, as the afternoon wore on it gradually dawned on me that, although *almost* everything was lost, it was not quite all. Krätschmer *et al.* had analysed their material by x-ray crystallography and not by NMR. So, the much-coveted single NMR line was still waiting to be observed. Thus I realised that there was just a single crumb of comfort left, but what a tasty morsel it would be and we should be able to observe it. (The NMR shift should also indicate just how aromatic the molecule was or was not. Of course the meaning of aromaticity for a species that cannot undergo substitution is debatable!) After all Jonathan had extracted the precious red solution on the Monday, four days before the extraction manuscript arrived on the Friday, and we also had the confirmatory 720-amu mass spectrum. So we already had material in our hands and we were the only ones apart from Krätschmer and collegues who had. We could also take immense intellectual satisfaction at having extracted the red solution before the arrival of the paper of Krätschmer and collegues. I suppose that that should be enough for a scientist—but of course it never is.

In 1982 Krätschmer and Huffman had observed puzzling UV absorption features while studying carbon dust produced by a carbon arc to simulate interstellar dust in the laboratory and measure the optical spectrum. After the publication of our discovery and theoretical predictions of the UV spectrum such as those by Rosen and co-workers (Larsson *et al.*, 1987; Braga *et al.*, 1991) and others (Weltner and Van Zee, 1989; Kroto, Allaf, and Balm, 1991), they conjectured that the features might be due to C_{60}. They then set about testing their idea by searching for the four tell-tale (IR) lines which theory suggested the molecule should exhibit (Disch and Schulman, 1986; Newton and Stanton, 1986; Wu *et al.*, 1987), Fig. 16. When they found them they went on to make C_{60} from pure ^{13}C and show that the isotope shifts were perfectly consistent with their conjecture (Krätschmer, Fostiropoulos, and Huffman, 1990a). They then extractred crystals, Fig. 20, and proved their conjecture conclusively. I look upon the conjecture that they had made C_{60} in 1982 together with the decision to test it by analysing their deposit by IR as one of the most prescient pieces of science I have ever come across and as time has progressed I have come to appreciate it more and more. The role played by spectroscopy—in both the initial UV observation and in particular the crucial tell-tale (IR) fingerprinting—is an archetypal example of the way spectroscopy can be used to solve important problems, in this case an historically significant one as well. To my mind there is no more amazing discovery than that there is a form of pure carbon that is *soluble*, and the image of the carbon crystals of Krätschmer *et al.*, shown in Fig. 20 has to be one of the most sublime images of 20th-century chemistry.

During the tea break that afternoon I showed the paper to my colleagues. Roger Taylor, offered to help us to get the one-line solution and immediately tried to extract as much material as he could from Jonathan who was somewhat reluctant to part with the small amount of the precious material that he had. Roger then made a key discovery: he found that the red solution could be chromatographically resolved into two components, one of which was red and the other a beautiful delicate magenta. (Chromatography has since become the accepted way to separate all the members of the fullerene family.)

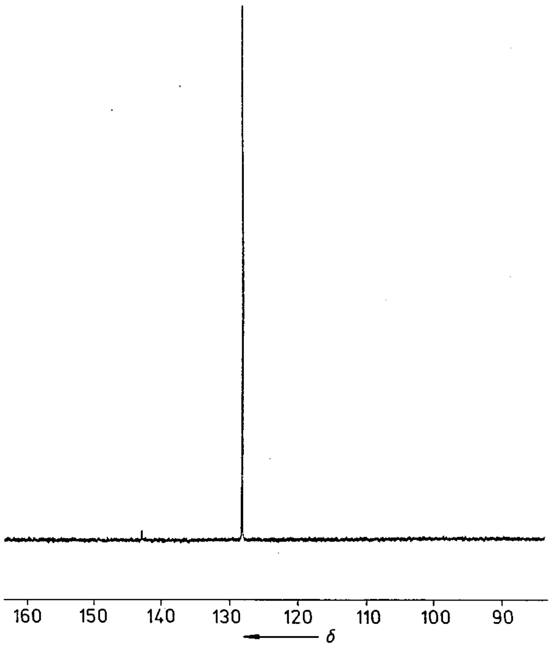


FIG. 21. The first NMR trace in which the C_{60} resonance (at 143 ppm was first identified (just!). The strong line at 128 ppm is (rather appropriately) the resonance of benzene.

Would NMR analysis show the single line? Tony Avent who operated the NMR spectrometer produced a two(?)-line spectrum from the magenta material (Fig. 21). One was magnificent strong line, but it was benzene—quite a well known compound. The second was a puny little blip in the base line, but Tony reckoned it was C_{60}, and he was right. To us it was the most beautiful little blip one could ever imagine. After further refinement the single line was observed as a strong signal (Fig. 23). The icing on the cake was the red material which gave five NMR lines—exactly what was expected for C_{60} (Fig. 22; Taylor *et al.*, 1990).

Thus in summary, Krätschmer, Lamb, Fostiropoulos and Huffman had indeed extracted C_{60} and at Sussex we had come a *very* close second. However Jonathan had extracted a red solution and Ala'a had detected a mass spectrum independently and before the Heidelberg/Tucson (*Nature*) manuscript had arrived. After this Roger had discovered the chromatographic separation of the fullerenes. Tony had detected the much coveted single line (Meijer and Bethune at IBM were also close and with Johnson also observed a single-line NMR spectrum (Johnson *et al.*, 1990). As a certain English football manager, noted for his "eloquence," in adversity would say—"The lads dun good!"

So in September 1990 some 20 years after the molecule was conceived by Osawa and five years after we

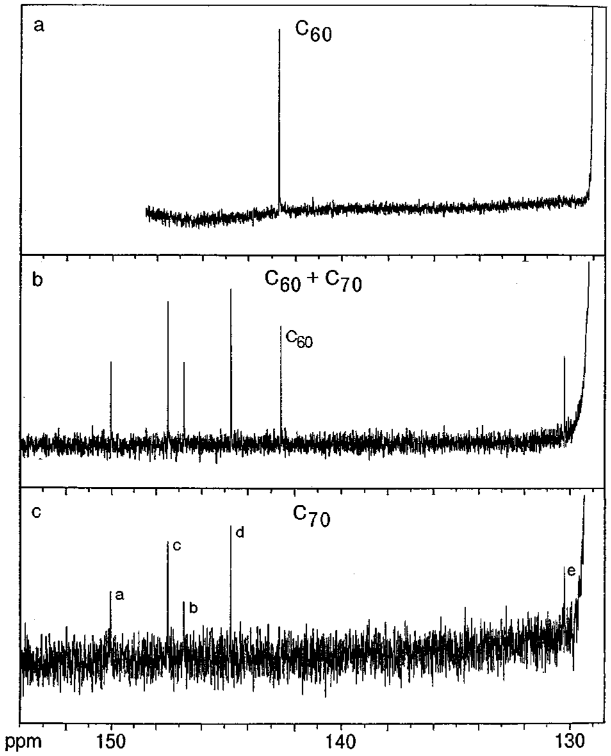


FIG. 22. C NMR spectrum obtained from chromatographically purified samples of soluble material extracted from arc-processes graphite: (a) spectrum of purified C_{60} (magenta fraction); (b) mixed sample; (c) spectrum of purified C_{70} (red fraction) showing five lines as expected for the symmetric egg-shaped molecule, Fig. 12.

had discovered that it could self-assemble, Krätschmer *et al.* had extracted it and Fullerene Science was well and truly on its way.

PHASE V. THE NEW ROUND WORLD OF FULLERENE CHEMISTRY, PHYSICS AND MATERIALS SCIENCE

After the extraction breakthrough in 1990, the field of fullerene research exploded and now some thousand papers a year are published in the field. Several new research projects, designed to explore the chemical and physical behaviour of the fullerenes, were launched at Sussex. With Roger Taylor and David Walton fullerene synthetic chemistry became a primary aim (Avent *et al.*, 1994). Roger Taylor and others pioneered the extraction of higher fullerenes C_{76}, C_{78} . . . etc. (Taylor, 1995). Spectroscopic studies were carried out with John Dennis and Jonathan Hare and also in collaboration with Sydney Leach and collegues in Meudon/Orsay. Halogenation studies have turned out to be particularly important, and Paul Birkett was able to show that $C_{60}Cl_6$ (Fig. 23) can form (Avent *et al.*, 1994). These observations, which may be considered to be the fullerene equivalent of ortho, meta and para direction in benzene, have been followed by the creation of some key acylated derivatives. Adam Darwish has probed a wide range of reactions in particular hydrogenation and hydroxylation reactions. Interesting mixed crystalline compounds involving ferrocene and phosphorus have been made and structurally characterised by Jonathan Crane, Wyn Locke and Peter Hitchcock (Avent *et al.*, 1994). Further chemical properties of C_{60} as a synthon, including for instance cycloaddition and metal complexation reactions, have been investigated by Mohammed Meidine, Brian O'Donovan and Martin van Wijnkoop, and solubilisation methods have been developed by Huang Shaoming. Colin Crowley and Andy Caffyn have been investigating thermolytic routes to C_{60}. Fragmentation behaviour is also being investigated with Perdita Barran, Steve Firth and Tony Stace (in collaboration with Eleanor Cambell of the Max Born Institute in Berlin). These studies followed on from the work of Simon Balm, Richard Hallet, Ken McKay and Wahab Allaf. Cold fluorescence studies are being carried out with Reg Colin, Pierre Coheur, Steve Firth, Michele Carlier (in Brussels) and Eleanor Cambell (in Berlin).

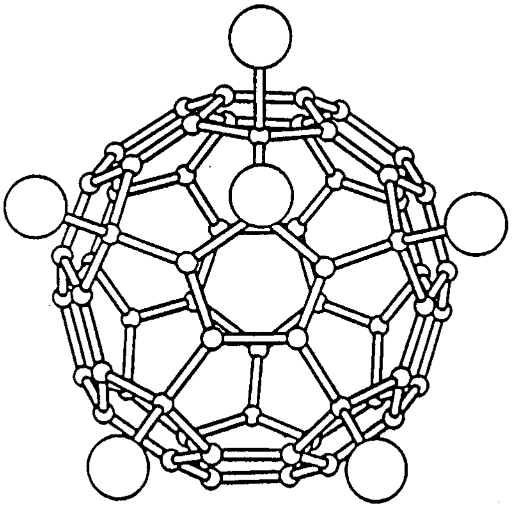


FIG. 23. The structure of $C_{60}Cl_6$ (Avent *et al.*, 1994).

A solid-state chemistry programme has been initiated by Kosmas Prassides in which fascinating solid-state dynamics and phase behaviour (Prassides, Christides, *et al.*, 1994) as well as superconducting properties of the metal intercalation complexes have been probed (Prassides, Vavekis, *et al.*, 1997). With Fred Wudl's group, the elegant azafullerenes are under detailed investigation (Prassides, Keshavarz-K, *et al.*, 1994).

On the nanotechnology front some fascinating advances have been made (Kroto, Hare, *et al.*, 1994). Collaboration with Morinobu Endo of Shinshu University in Japan has opened up several new avenues in the creation of nanostructions by pyrolytic methods and possible nanotube growth mechanisms. With Mauricio Terrones, Wen Kuang Hsu and Jon Hare, the fascinating way that nanostructure creation is governed by metal-cluster catalysts is being investigated (with Umberto Terrones in Mexico). Related investigations of these promising routes to nanoscale materials are under way with Thomas Müller, Doug Reid and Nicole Grobert. Wen-Kuang Hsu has observed the amazing result that nanotubes can be obtained by electrolysis (Kroto, Hare,

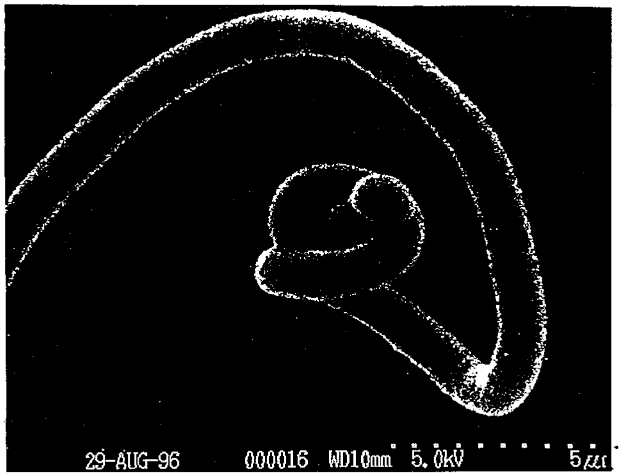


FIG. 24. Thermolytically created carbon nanostructure.

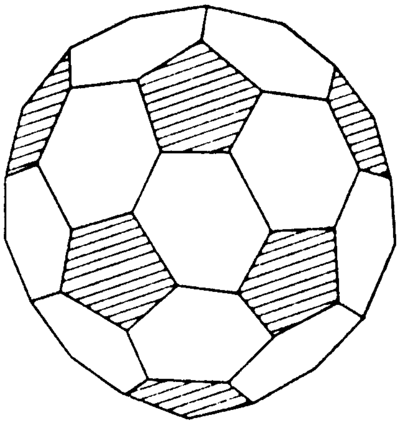


FIG. 25. The first image of C_{60} ever published (Osawa, 1970; Yoshida, and Osawa, 1971). Taken from Yoshida and Osawa, 1971.

et al., 1994). Just as exciting as the new carbon structures are the boron nitride nanotubes. Some of this nanotechnology work is being carried out in collaboration with Tony Cheetham and Xing Ping Zhang at UCSB and Laurence Dunne at the University of the South Bank. All in all the way ahead looks exciting, as is exemplified by the nanostructure shown in Fig. 24, which appears very much like an extra which has escaped from the set of the film Alien II.

EPILOGUE. THE COSMIC AND MICROCOSMIC CHARISMA OF THE SOCCERBALL

One cannot end any account of the discovery of C_{60} without noting that it has the same structure as a foot-

FIG. 26. This photograph of Ellis captures perfectly the delight that C_{60} can stimulate in youngsters of all ages (photographer, G. E. Watson, published with permission).

ball (or soccerball) and that this led to its original conception. Thus it seems fitting to reproduce in Fig. 25 the image from the book by Osawa and Yoshida (Yoshida and Osawa, 1971) and point out that much of the world now plays football (or soccer). Furthermore a large number of researchers are studying the peculiar behaviour of the ball on a microcosmic scale. Last but not least we should note that, perhaps, the molecule's most delightful property lies in the inherent charisma (Kroto, 1994) which arises from its elegantly simple and highly symmetric structure that is quite unlike any other. It is this charisma that has stimulated delight and fascination for chemistry in young and old alike. Perhaps no image captures the most important quality of C_{60} better than the photograph depicted in Fig. 26. It says it all.

ACKNOWLEDGMENTS

There are many people to whom I owe deep debts of gratitude in addition to the students, collegues and friends who appear in the above text. I thank in particular those students who were not directly involved with C_{60} related studies because much of their work formed a basis to which many ideas may be tenuously traced. The support over the years has come from several sources, mainly the School of Chemistry and Molecular Sciences of the University of Sussex, SRC, SERC, EPSRC, NATO, The Royal Society, BP (John Cadogan), ICI/Zeneca (Peter Doyle, Mike Hutchinson, Neil Winterton), British Gas and BOC (Steve Wood) and Alfred Bader.

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