Dawn of the fullerenes: experiment and conjecture*

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CONJECTURE

Several individuals in widely separated parts of the world had envisioned the class of carbon-cage compounds we now know as the fullerenes, in particular C_{60}, long before we began our work. The earliest reference in the area appears to be the somewhat whimsical proposal by Jones (1966) that giant carbon-cage molecules, which we would now call giant fullerenes, might be synthesized by introducing defects in the graphitic sheet to allow them to curve and close. He believed that such molecules should exhibit unique properties such as having a very low density. He realized some time later that the required defects would be pentagons (Jones, 1982).

Apparently the first person to imagine the truncated icosahedron isomer of C_{60} shown in Fig. 1 was Osawa (Osawa, 1970; Yoshida and Osawa, 1971). Osawa conceived of the C_{60} structure while meditating on the structure of corannulene ($C_{20}H_{10}$), which has a central pentagon of carbon atoms surrounded by five hexagons, when he glanced at his son's soccer ball (football) and recognized the same pattern. Shortly thereafter a Hückel treatment of the pi electrons was carried out in the Soviet Union (Bochvar and Gal'pern, 1971) and repeated independently some years later in the USA as part of a larger article (Davidson, 1981). The Hückel calculation was repeated again by Haymet in his discussion of the stability of the molecule (Haymet, 1986).

The synthetic organic chemist Orville Chapman took the challenge of the synthesis of truncated icosahedron C_{60} seriously in the early 1980s, obtained funding from the National Science Foundation for this purpose, and set to work with several graduate students on its total synthesis (Baggot, 1994). This project is indeed a tremendous challenge to the conventional methods of organic synthesis, and to date no such total synthesis of C_{60} has been completed.

These conjectures concerning C_{60} were based upon good chemical intuition backed up by approximate quantum chemical calculations. The conclusion of these conjectures was that truncated icosahedron C_{60} would be a chemically stable compound that, once prepared, could be handled much as any common substance.

EXPERIMENT

When we started our experiments on carbon clusters in late August 1985, we were completely ignorant of the conjectures just related. The purposes of our carbon cluster project were to determine whether the sort of carbon-chain compounds such as HC_7N found by radioastronomy in the interstellar medium (Kroto *et al.*, 1978; Avery, 1979) could be synthesized by mixing carbon vapor with a suitable reagent such as ammonia and to find the conditions needed for a study of the low-temperature electronic spectra of carbon-chain compounds using resonance-enhanced two-photon ionization. The spectroscopic work on carbon chains was motivated by the proposal made by Douglas (1977) that electronic absorptions of long-chain carbon molecules, $C_n (n = 5-15)$, are the source of the diffuse interstellar bands (Herbig, 1975). The work on formation of carbon chain compounds was ultimately published (Heath *et al.*, 1987; Kroto *et al.*, 1987) but the carbon-chain spectroscopy was never really begun.

I won't review in detail here the experiments we carried out in August and September of 1985 which resulted in our proposal (Kroto *et al.*, 1985) that truncated icosahedron C_{60} (buckminsterfullerene) is formed spontaneously in condensing carbon vapor. Accounts of this have been given by two of the five people involved (Smalley, 1991; Kroto, 1992) and in two books on the discovery of the fullerenes (Baggot, 1994; Aldersey-Williams, 1985). The authors of these books consulted all five of us and, in my opinion, made the best effort possible to use the recollections of those involved to recreate these events.

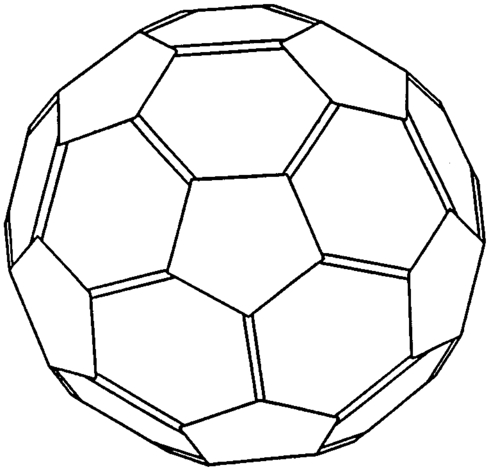

FIG. 1. Truncated icosahedron C_{60} with dominant Kekulé structure.

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

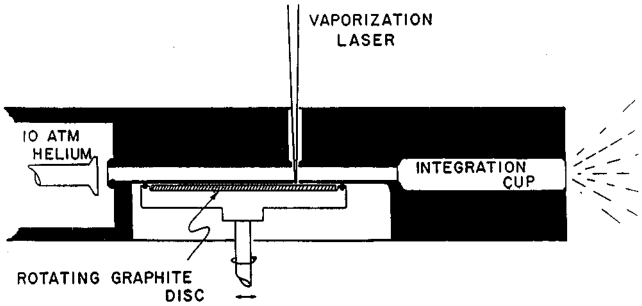

FIG. 2. Laser vaporization source for producing molecular beams of clusters of refractory materials. The integration cup can be removed. For the carbon experiments, the target is a graphite disk which is rotated slowly to provide fresh vaporization surface. The vaporization laser, a 5 ns pulse at 532 nm of about 30–40 mJ, is focused onto the surface of the graphite. The pulsed nozzle passes helium over this vaporization zone.

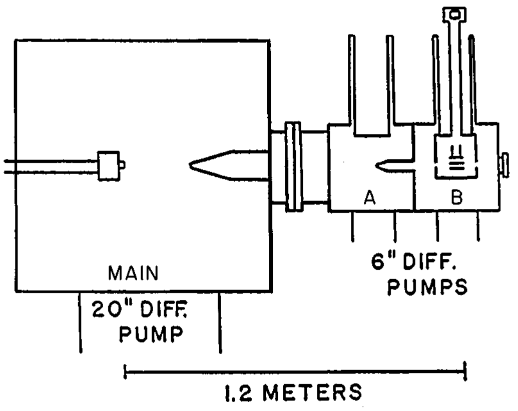

FIG. 3. Molecular-beam photoionization time-of-flight mass spectrometer.

However, in order to understand what we did it is necessary to learn something about the apparatus invented by Richard Smalley (Dietz *et al.*, 1981; Powers *et al.*, 1982; Hopkins *et al.*, 1983) to investigate compounds and clusters formed from refractory elements. He and his students used it to investigate the high-resolution electronic spectra of a number of metal dimers (Michalopoulos *et al.*, 1982; Powers *et al.*, 1982; Hopkins *et al.*, 1983; Landridge-Smith *et al.*, 1984), copper trimer (Morse *et al.*, 1983), and SiC_2 (Michalopoulos *et al.*, 1984). In 1984, Frank Tittel, Smalley, and I with our students began investigating semiconductor clusters using this apparatus.

The heart of the experiment is the laser vaporization supersonic molecular-beam source. The source went through several design variations primarily to accommodate the physical form of the available sample material to be vaporized. For these experiments, it was a disk vaporization source because the semiconductor samples that we had been investigating were more readily available in sheet form. Figure 2 shows a cross section of this pulsed molecular-beam source. In operation, the solenoid-actuated pulsed valve was fired to release through the 1 mm orifice a pulse of He gas over the sample lasting somewhat less than a millisecond. The backing pressure could be as high as 10 atm. At some point during the gas pulse, usually near its middle, the Q-switched frequency-doubled vaporization laser was fired generating a 5-ns long pulse of green light (532 nm) with an energy of roughly 30–40 mJ. This laser was focused onto the rotating-translating graphite disk (to avoid digging pits into the sample), vaporizing a plume of carbon vapor into the gas stream. Multiphoton ionization and the subsequent heating of the resulting plasma limited the amount of material vaporized in a single shot and insured that the species initially contained in it were atoms or very small molecules such as C_2 and C_3.

The material vaporized was caught up in the helium gas flow, was mixed with it and cooled by it. The cooling vapor then began to condense into clusters. The extent of clustering could be varied by changing the backing pressure, the timing of the firing of the vaporization laser with respect to the center of the gas pulse, and by varying the length and geometry of the channel downstream from the vaporization point. In the configuration shown in Fig. 2, an integration cup has been added to the end of the gas channel to provide more time for clustering and reaction before supersonic expansion.

After clustering, the gas pulse was expanded supersonically through a nozzle into a large vacuum chamber (see Fig. 3). Because this expansion is essentially an adiabatic reversible expansion, the temperature of the species in the gas drops from somewhat above room temperature to a few degrees Kelvin. After a few dozen expansion-nozzle diameters, collisions between particles in the expansion jet cease resulting in gas stream with a narrow, highly directional velocity distribution. The resulting jet of cold clusters can be skimmed into a molecular beam and interrogated by mass spectrometry. Mass-spectrometric detection labels the species by mass, which is a particularly important consideration in the study of clusters where a wide distribution of cluster sizes is always found. In addition, mass-spectrometric detection provides high sensitivity and permits extensive control of the trajectory of the cluster ions. Consequently, a variety of methods for manipulating and probing the cluster ions were developed and used in this work. These more sophisticated methods will be described later at the appropriate point. For the present, we focus on the simplest mass spectrometry.

For mass-spectrometric detection, the skimmer at the end of the large chamber forms a molecular beam from the portion of the jet moving directly away from the nozzle. This beam is passed through a differential pumping chamber and another skimmer and thence between the plates of the ion extraction field. In the most usual experiments, this field is a DC field and ions are produced by a pulsed ionization laser (normally an ArF 193 nm excimer laser, 6.4 eV, pulse length about 10 ns). Once produced the ions are accelerated by the DC field into the drift tube of a time-of-flight mass spectrometer. Because all ions of unit charge receive the same energy, ions of greater mass reach a final velocity that is less than ions of lesser mass. Therefore the mass of the ion in

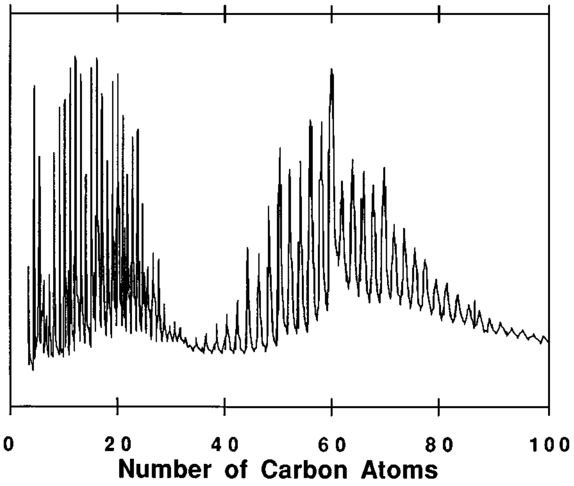

FIG. 4. Carbon cluster distribution observed under mild clustering conditions. This distribution is similar to that obtained by Rohlfing, Cox, and Kaldor (1984).

the acceleration region is determined by its time of arrival at the ion detector. By plotting ion detector signal vs arrival time, a mass spectrum of the cluster distribution is obtained. Often these cluster distributions are quite colorful, exhibiting "magic number" cluster sizes where a peak is more prominent than its neighbors by a factor of perhaps two. Figure 4 shows a cluster distribution for carbon similar to that obtained previously by Rohlfing, Cox, and Kaldor (1984) with essentially the same apparatus. In the Rohlfing, Cox and Kaldor distribution, C_{11}^+, C_{15}^+, C_{19}^+, and C_{60}^+ might be called magic numbers. The discovery of the fullerenes began when we found that under the right conditions, C_{60}^+ could become a super magic number far more prominent than its neighbors.

When the carbon system was investigated in September 1985, major fluctuations in the prominence of the C_{60} peak compelled us to examine this mass region more carefully under a variety of clustering conditions. It was found that the relative prominence of the C_{60} mass peak could be varied from roughly twice the intensity of its nearest neighbors to about 50 times the intensity of its nearest neighbors. This led us to propose that the very prominent C_{60} cluster we had observed has a closed, highly symmetric, carbon-cage structure in the form of a truncated icosahedron (Kroto *et al.*, 1985). Since our inspiration to look for a spherical-cage structure came from the geodesic domes of R. Buckminster Fuller, we dubbed this molecule buckminsterfullerene.

The buckminsterfullerene proposal rested on the single experimental observation that carbon-vapor condensation conditions could be found where the intensity of the mass spectrum peak of the C_{60} in the carbon cluster beam was many times the intensity of any of its near neighbors in mass as shown at the top of Fig. 5. Was this proposal a lucky guess or is this single observation, taken in context, sufficient to prove that the prominent C_{60} peak in Fig. 5 is the truncated icosahedron isomer shown in Fig. 1? Our claim has always been that the situation is much closer to proof than conjecture.

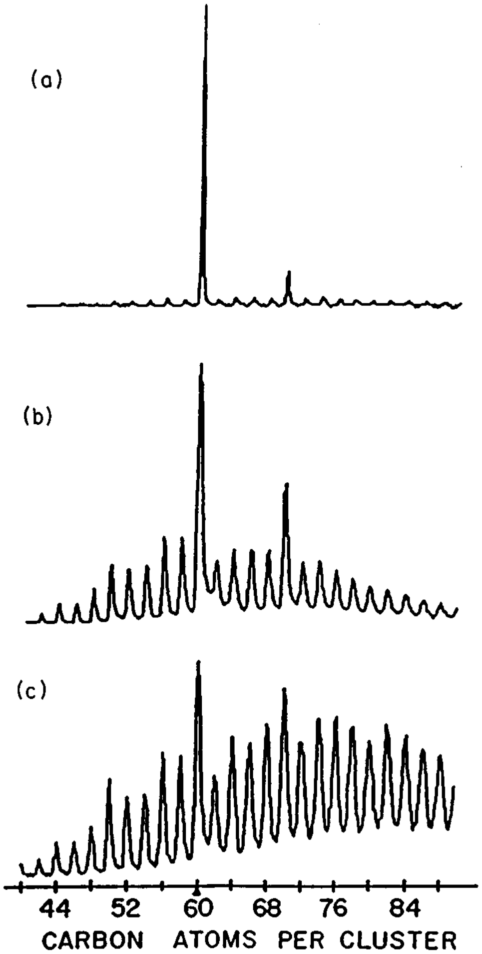

FIG. 5. Mass spectrum of the C_{60} mass region showing C_{60} growing prominent. Panel (c) corresponds to a situation where the helium backing pressure is low and there is no integration cup. Panel (b) was obtained with full helium backing pressure with vaporization in the center of the gas pulse, but no integration cup. Panel (c) has the integration cup in addition to full helium backing pressure.

Note in Fig. 5 that the relative prominence of C_{60} depends upon the clustering conditions. The C_{60} peak becomes more prominent when more time is given for high-temperature (room temperature and above) collisions between the carbon clusters. This immediately indicates that whatever isomer(s) of C_{60} are responsible for its prominence must be "survivors" that are relatively impervious to chemical attack.

There are probably millions of plausible isomers of C_{60}, which differ in chemical connectivity. Most of these millions of C_{60} isomers will be obviously chemically reactive, with dangling carbon bonds, and thus unable to survive chemical attack. The role of chemical attack is manifested in the fact that in all three distributions in Fig. 5 only even carbon clusters are observed in contrast to observations not shown here, but shown in Fig. 4, of the region below 25 carbon atoms where both even and odd clusters are observed with comparable intensities. It is possible to find clustering conditions where both even and odd carbon clusters are observed with comparable intensity near C_{60}; these conditions correspond to much less time for chemical reaction than for any of the mass spectra shown in Fig. 5. Such a distribution is shown in Fig. 6. Thus even in the bottom panel of Fig. 5 the observation of clusters with only even carbon numbers is evidence that already all the clusters in the region must have some special structures that are less susceptible to chemical attack than a typical dangling-bond isomer. As will be discussed below, the obvious explanation from our present viewpoint is that these clusters are all closed carbon-cage structures (fullerenes) also. In September 1985, we recognized, without the fullerene concept, that the even-cluster distribution probably reflected isomers of reduced reactivity compared with the odd clusters.

Thus we believed that the very prominent C_{60} peak in the top panel of Fig. 5 could be explained only by a single isomer of C_{60} remarkably impervious to chemical attack. A readily imaginable alternative explanation would be in terms of a C_{60} isomer that is much easier to photoionize than its neighbors by the 6.4 eV ArF ionization laser employed. However, this explanation ignores the clear increase of the prominence in the C_{60} signal when more time is allowed for chemical reaction. Thus an explanation for the prominence of C_{60} based on its easier photoionization does not take into account the obvious reduced chemical reactivity of C_{60} compared with its neighbors. Further evidence against an explanation based upon photoionization efficiency was obtained in later experiments that demonstrated a similar prominence of C_{60}^+ upon photoionization with a 7.9 eV F_2 excimer laser (Liu *et al.*, 1986).

The truncated icosahedron form of C_{60} is clearly a special structure that should be chemically very stable. It has no dangling bonds, with the valences of every atom satisfied. The pattern of double and single bonds depicted in Fig. 1 is just one of 12500 possible Kekulé structures (Klein *et al.*, 1986) (but it has proved to be the dominant one). By symmetry, every atom is equivalent so that there is no specific point of chemical attack. Strain is introduced in curving the intrinsically planar system of double bonds into a spherical shape, but the strain is symmetrically and uniformly distributed over the molecule, thereby again avoiding a weak point for chemical attack. There is obviously no other structure with this high degree of symmetry, and very little reason to fear that another structure could be found that offers this unique combination of advantages. For these reasons, and in spite of the fact that it seems very counterintuitive for this high symmetry, low entropy molecule to form out of the chaos of carbon vapor condensing at high temperature, we have never really considered the assignment of the prominent C_{60} peak in the mass spectrum to the buckminsterfullerene structure to be a guess.

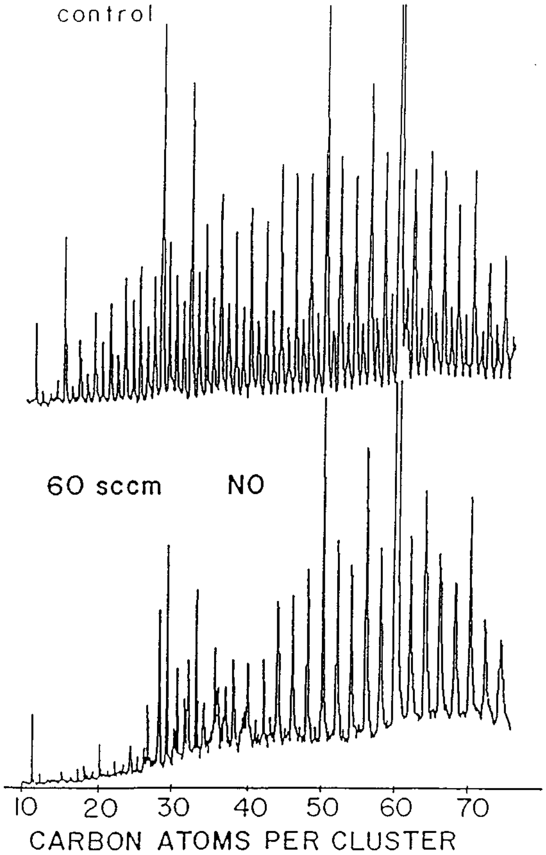

FIG. 6. Reaction of carbon clusters with NO. The upper control mass spectrum was obtained without added NO. In the lower spectrum roughly 1 Torr of NO was added to the gas stream in the fast-flow reaction tube. It is clear that the odd clusters react with NO. The various products of these reactions are not resolved, but contribute to the elevated baseline seen in this spectrum.

In science, more proof is always demanded. Later experiments (Liu *et al.*, 1986; O'Brien *et al.*, 1986) demonstrated that the special prominence of C_{60} was not the result of some special preference for the C_{60}^+ ion upon photofragmentation and that C_{60} can be made specially prominent in both the residual cations and anions (a residual ion being an ion that is formed in the vaporization plasma and survives the expansion process).

CONJECTURE—THE FULLERENE HYPOTHESIS

We soon learned from Haymet's paper (1986) of Euler's rule (1752/3) stating that a solid figure with any even number n of 24 or more vertices could be constructed with 12 pentagons and $(n - 20)/2$ hexagons. This immediately provides an explanation in terms of such carbon-cage molecules of the even cluster distribution that appears at carbon numbers above 30 in the mass spectrum, as these molecules would have no dangling bonds and would thus be relatively unreactive. These spheroidal carbon-cage carbon molecules consisting only of pentagons and hexagons were given the generic name of fullerenes.

However, in contrast with the truncated icosahedron explanation for the prominent C_{60} peak, this conclusion has always seemed to me to be much more conjecture, however plausible. The next few years of our lives were

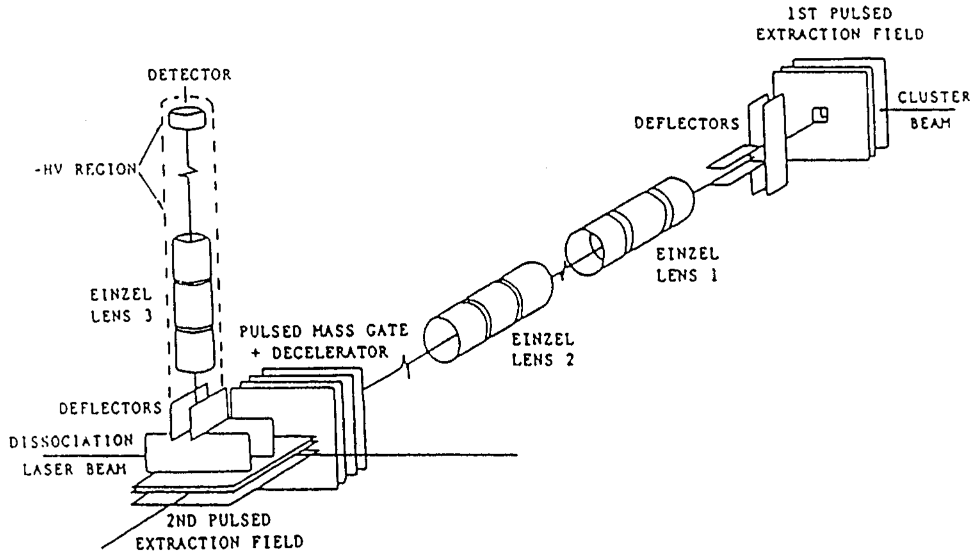

FIG. 7. Tandem time-of-flight mass spectrometer. The molecular beam containing residual ions from the vaporization plasma enters the extraction region of the primary mass spectrometer where a 2000 V pulse is applied across the grids. The deflectors remove the molecular beam velocity. The einzel lenses focus the ion beam. Ions are selected by the mass gate and then fragmented by the laser and analyzed by the second time-of-flight mass spectrometer.

devoted to testing experimentally this fullerene hypothesis and finding that it passed every test.

EXPERIMENT—REACTIVITY AND PHOTOFRAGMENTATION

It is possible to inject chemical reagent gases into the cluster stream prior to the expansion and then to observe reaction-product ions in the mass spectrum (Geusic *et al.*, 1985; Morse *et al.*, 1985). A reaction tube was added to the end of the cluster source and various reagents, such as NO, SO_2, NH_3, H_2, CO, and O_2 were injected into the gas stream (Zhang *et al.*, 1986). It was possible to obtain a mass distribution without added reagent that showed both odd and even carbon-number peaks with the odd carbon-number peaks about half the intensity of the even ones. When a reagent such as NO or SO_2 was added, the odd carbon-number peaks disappeared, but the even carbon peaks with 40 atoms or more remained unreactive as would be expected if they were fullerenes having no dangling bonds. The distributions observed in this experiment are shown in Fig. 6. Note that the odd clusters, which are believed to have dangling chemical bonds, are much more reactive than the even clusters.

A series of photofragmentation experiments was carried out on the carbon-cluster ions hypothesized to be fullerenes using a tandem time-of-flight mass spectrometer (O'Brien *et al.*, 1988). The apparatus is shown in Fig. 7. In these experiments, a single carbon-cluster ion was mass selected and then interrogated by a photofragmentation laser as shown in the apparatus detail, Fig. 8. It was then accelerated into a second time-of-flight drift region and the mass of its ionic fragments determined. The photofragmentation pattern of C_{60}^+ is shown in Fig. 9. As can be seen, the fragmentation pattern corresponds to the loss of an even number of carbon atoms down to C_{32}^+ where it changes abruptly to produce ions containing about 20 atoms. We believe that C_{60}^+ is losing an even number of carbon atoms in a few step process with the fullerene cage of the ion reclosing upon loss of the neutral even-number fragment. The abrupt change in pattern at C_{32}^+ takes place because the strained small fullerene can no longer close upon carbon loss and instead a large neutral fragment is shaken off when the strain energy is suddenly released upon opening the cage.

The energies of many of the fullerenes have been calculated at the STO-3G/SCF level of theory by Scuseria

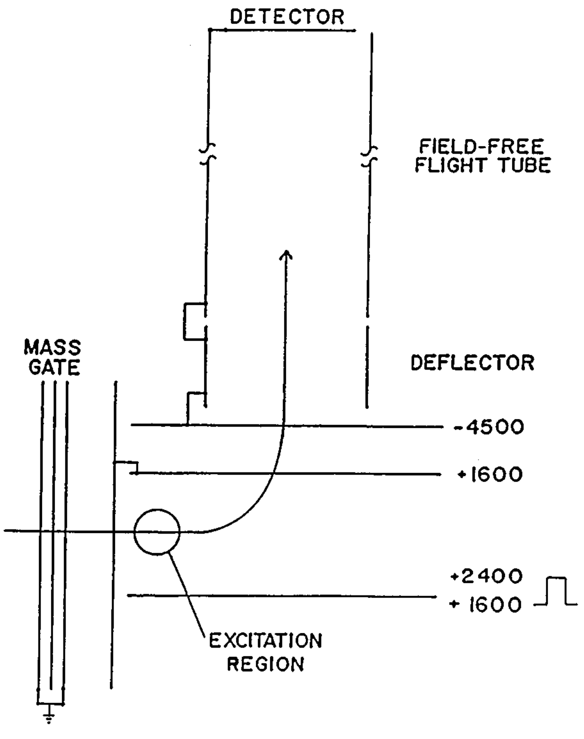

FIG. 8. Detail of the photofragmentation region of the tandem time-of-flight apparatus showing the mass gate, laser excitation region, extraction optics, and flight tube.

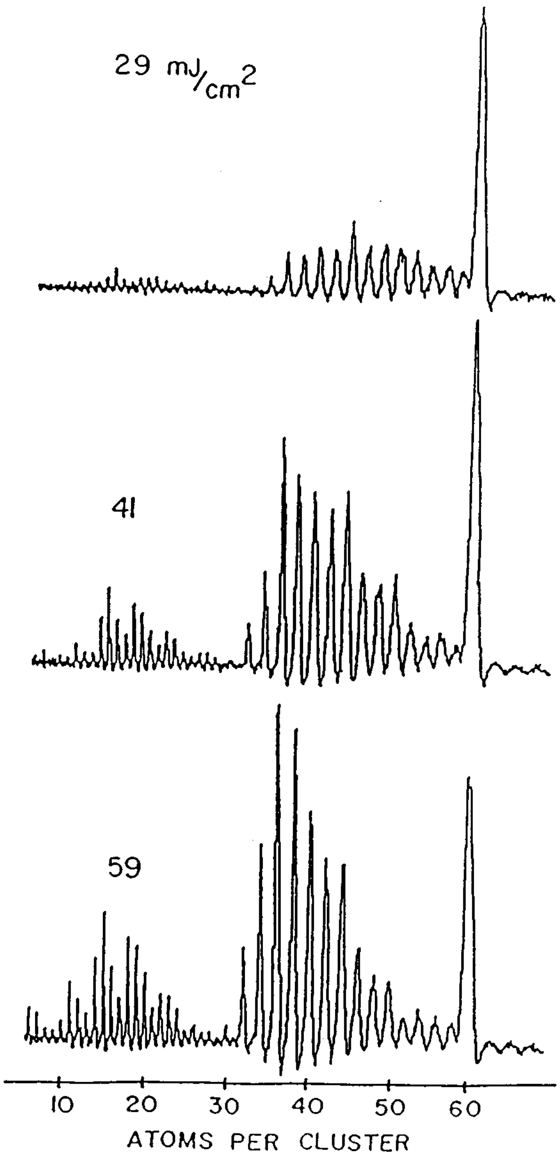

FIG. 9. Photofragmentation pattern of C_{60}^+ showing loss of even number of carbon atoms and breakoff at C_{32}^+.

(Murry *et al.*, 1994) and are shown in Fig. 10. It should be noted that for fullerenes of size C_{28} and larger there is more than one fullerene structure for a given number of carbon atoms (Fowler and Manopoulos, 1995). For example, there are 1812 fullerene isomers (i.e., cages containing 12 pentagons and 20 hexagons) of C_{60} alone (Manopoulos, 1992; Liu *et al.*, 1992). The energies plotted in Fig. 10 are for the lowest-energy fullerene isomers found. Truncated icosahedron C_{60} and D_{5h} symmetry C_{70}, which are respectively the lowest-energy fullerene isomers of 60 and 70 carbon atoms, are local minima in the energy curve, and this can be strikingly seen in these energetics. We label the buckminsterfullerene isomer of C_{60} ,C_{60}^{BF}.

When these energies are combined with the bond-dissociation energy of C_2 (Huber and Herzberg, 1979) of 6.21 eV, the overall energy change in fragmentation can be calculated. Thus the overall energy change in

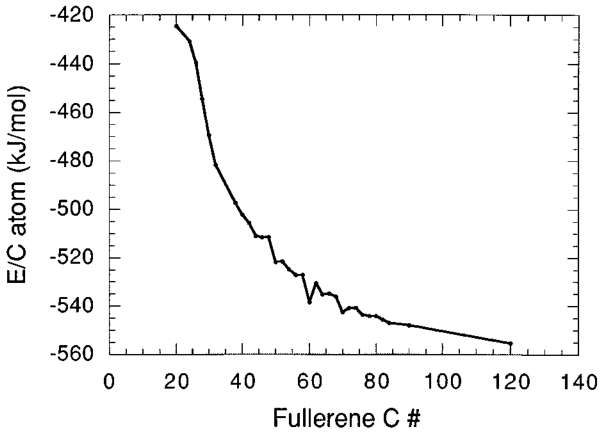

FIG. 10. Energy per carbon atom relative to atomic C as a function of fullerene cluster size at the STO-3G/SCF level at the MM3 optimized geometry for the lowest-energy fullerene structure for each size. This figure is based upon the calculations of R. L. Murry, D. L. Strout, and G. E. Scuseria (1994).

$$C_{62}\rightarrow C_{60}^{BF}+C_2 \tag{1}$$

is $\Delta E = 0.7$ eV, while for the loss from C_{60}^{BF}

$$C_{60}^{BF}\rightarrow C_{58}+C_2 \tag{2}$$

$\Delta E = 11.2$ eV. The activation barrier for the fragmentation of C_{60} cannot be less than the fragmentation energy of 11.2 eV. In order to have substantial fragmentation of C_{60}^{BF+} in the few microseconds available in Fig. 9, I estimate that about 100 eV must be deposited into the C_{60}^{BF} ion.

If the activation barriers to fragmentation follow the energetics, one would expect that the special stability of C_{60}^{BF} would be apparent in the fragmentation pattern. Figure 11 shows fragmentation of some larger clusters when the sample is irradiated just before the acceleration region of the second time-of-flight mass spectrometer as shown in Fig. 9. Only a few microseconds are available for fragmentation after irradiation and before acceleration and analysis, and C_{60} and C_{70} are only slightly special fragments. However, if the irradiation is carried out in the *first* time-of-flight extraction region just before extraction and the ions that have the right time-of-flight for the initial species of Fig. 12 are permitted through the mass gate, the pattern is much different. Here the sequence is that the large ion is irradiated and accelerated before it fragments; it then has time to fragment all the way to the second extraction region which corresponds to a time of about 120 μs.

In Fig. 12, it is clearly seen that C_{60} is quite prominent. The original ion is less energetic than is the case of the short-term fragmentation and thus the fragmentation pattern is much more sensitive to the fragmentation energetics. The relationship between the long-time fragmentations of Fig. 12, where C_{60}^+ is very prominent, to the short-time fragmentations of Fig. 11, where C_{60}^+ is less prominent, can be explained if one assumes that the activation barriers to ring rearrangements on the surface

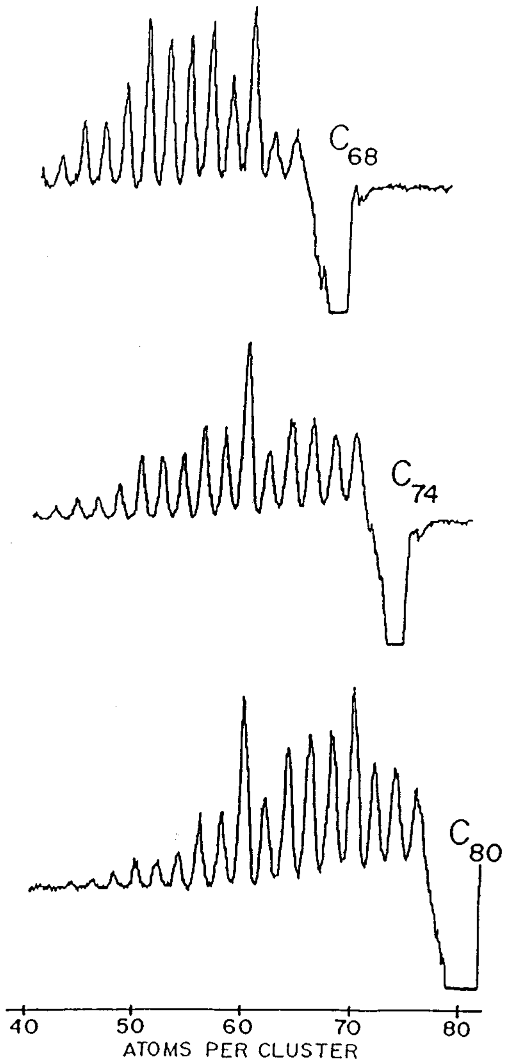

FIG. 11. ArF ($15\ \mathrm{mJ\ cm^{-2}}$) fragmented large even-carbon clusters. There is no difference in the fragmentation pattern of the large clusters. C_{60} and C_{70} are slightly favored.

of the fullerene ions are much less than the activation barrier to fragmentation of a typical fullerene ion.

Assume that a fragmentation that leads to a C_{60}^+ fullerene takes place. It is unlikely that this C_{60} ion has the buckminsterfullerene structure. Probably several rearrangements of this ion must take place before the especially stable C_{60}^{BF} structure is found. When long-time fragmentation is investigated, there is sufficient time for a number of lower activation energy ring rearrangement processes to take place before fragmentation because the energy deposited in the original ion is relatively small compared with the short-time fragmentation energy. These ring rearrangements find the low-energy buckminsterfullerene structure, which is very hard to fragment. With the short-time fragmentation, far more energy is deposited in the original ion and fragmentation occurs before the low-energy buckminsterfullerene structure is found.

Figures 9, 11, and 12 taken together provide striking evidence that the cations being examined are structurally related to each other and to C_{60}^{BF}. It appears that fragmentation takes place with the preservation of the cage structure until the breakoff point at C_{32} is reached.

CONJECTURE—THE EXISTENCE OF ENDOHEDRAL COMPLEXES

The fullerenes are hollow. Buckminsterfullerene has a cavity almost 4 Å in diameter that is capable of holding any atom of the periodic table. It seemed to us that it might be possible to introduce a foreign atom into the central cavity to produce an endohedral adduct. We recognized that bulk samples of such materials, if they could be obtained, might have many unusual and potentially useful properties. For this narrative, the important point is that such an endohedral atom would be difficult to dislodge.

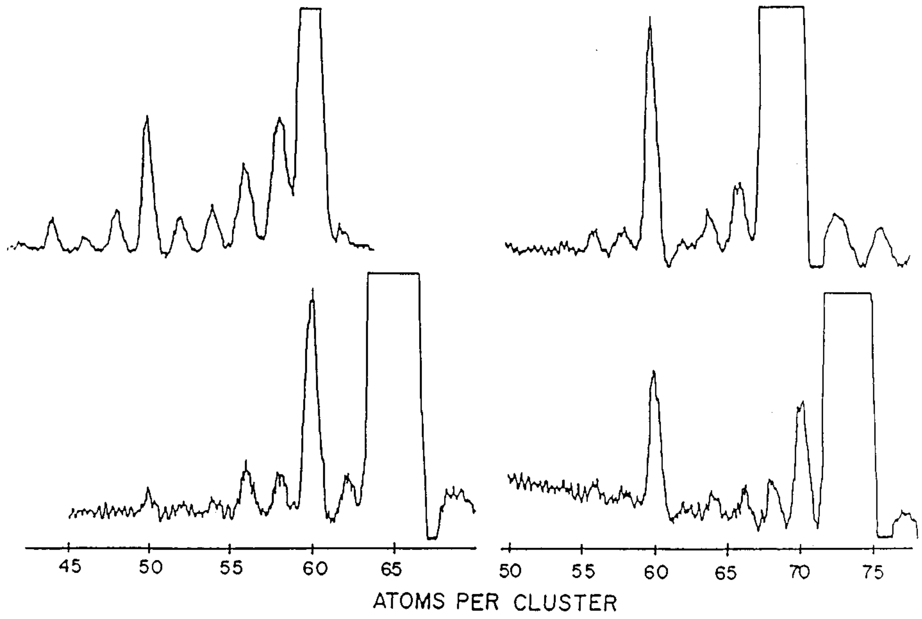

FIG. 12. Metastable time-of-flight mass spectra for 60, 66, 70, and 74 atom clusters. The clusters were irradiated 1 μs before the first extraction pulse with $15\ \mathrm{mJ\ cm^{-2}}$ ArF. The ions were mass gated at the time appropriate to the parent ions listed above and analyzed in the second time-of-flight mass spectrometer. The travel time to the second mass spectrometer was approximately 120 μs. The special prominence of C_{60} and C_{70} is clear.

EXPERIMENT—ENDOHEDRAL METALLOFULLERENES AND "SHRINK WRAPPING"

Success in forming adducts with a single lanthanum atom was almost immediately achieved (Heath *et al.*, 1985). In these experiments, a low-density graphite disk was soaked in a water solution of $LaCl_3$, dried and used as target for laser vaporization. The mass spectrum at low ionization laser fluence showed many peaks from both pure carbon and carbon-lanthanum adducts, but when the ionization laser power was turned up somewhat so that the least stable species would photofragment, all bare cluster peaks except for C_{60} and C_{70} disappeared, but clusters with one lanthanum atom at every even carbon number remained. There were no clusters remaining with more than one La atom. Thus under laser fluences capable of destroying the less stable carbon clusters, one and only one lanthanum atom stuck. This is a strong indication that the lanthanum atom is inside the cage.

It was found that endohedral metallofullerenes containing the alkali atoms K and Cs could be readily formed. This led to a unique way to test the fullerene hypothesis by "shrink wrapping." A series of photofragmentation experiments was carried out (Weiss *et al.*, 1988) in a Fourier-transform ion cyclotron resonance cell on $C_{60}K^+$ and $C_{60}Cs^+$. A supersonic beam of cluster ions is prepared as described above and injected into the ion cyclotron resonance cell where they can be trapped for several minutes. By applying a range of rf frequencies to the cell, the orbits of almost all ions but the desired one, $C_{60}K^+$ (or $C_{60}Cs^+$), can be excited thereby driving the unwanted ions from the cell. Photofragmentation experiments can then be carried out on the remaining ions.

From our previous experiments on photofragmentation and $C_{60}La^+$, we expected that at low laser fluences the ions would lose C_2, C_4, and C_6, while retaining the metal. If the metal is in the cage as proposed, the cage will become increasingly strained upon loss of neutral carbon because it is shrinking down upon the resistant metal core. A point will be reached where the cage will break, releasing the metal. This point will depend upon the size of the metal ion and will therefore be reached for larger clusters in the case of $C_{60}Cs^+$ than in the case of $C_{60}K^+$. Furthermore, the cage-breaking point can be roughly estimated from the van der Waals radii of the alkali ion and the carbon atoms. Figure 13 shows the photofragmentation results. The even-carbon loss breaks off for $C_{60}K^+$ at $C_{44}K^+$ and for $C_{60}Cs^+$ at $C_{48}Cs^+$, which agrees well with predictions from the van der Waals radii. We can conceive of no explanation for these observations other than that we were observing fragmentation of endohedral fullerene complexes.

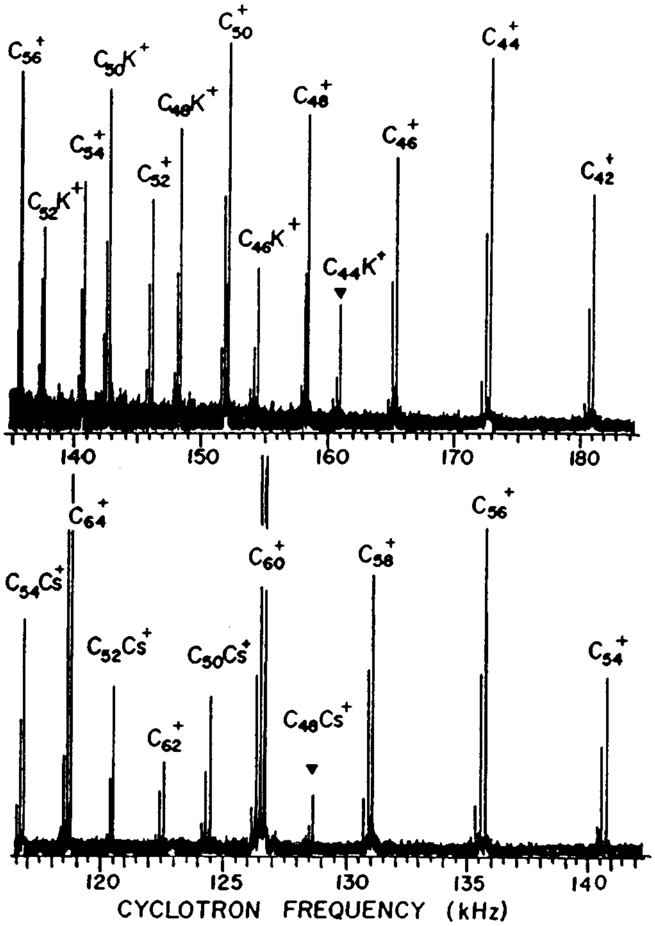

FIG. 13. The low-mass portion of the fragment ions produced by intense laser excitation of $C_{60}K^+$ (panel A) and $C_{60}Cs^+$ (panel B) in the Fourier-transform ion cyclotron resonance trap. The clusters containing carbon only seen in these spectra arise from fragmentation of empty fullerene ions simultaneously trapped with the metal species.

CONJECTURE—C_{70} HAS D_{5h} SYMMETRY

In almost all mass spectrometer carbon-cluster distributions where C_{60}^+ (or C_{60}^-) is prominent, C_{70}^+ (or C_{70}^-) is usually the next most prominent ion in the C_{40}–C_{90} mass range. Therefore it is likely to have a somewhat special structure. A plausible guess for the structure of C_{70} seemed to be one in which a band of five hexagons was added around the equator of C_{60} (Heath *et al.*, 1985). To form such a structure (see Fig. 14), choose an orientation of C_{60} so that pentagons are at the north and south poles; then cut the C-C bonds connecting the northern and southern hemispheres, separate them, rotate one hemisphere by 1/10 turn with respect to the other and add a string of 10 carbon atoms at the equator to rejoin the two hemispheres.

Both the structures of C_{60}, buckminsterfullerene, and $D_{5h}C_{70}$ have no abutting pentagons. Haymet suggested that such connected rings would be destabilizing (Haymet, 1986). Shortly thereafter, Schmalz *et al.* (1986) pointed out that abutting pentagons necessarily involve destabilizing, antiaromatic eight atom conjugated pi electron circuits around the ring making structures with abutting pentagons less stable. Both Kroto (1987) and Schmalz *et al.* (1988) proposed that $D_{5h}C_{70}$ is the smallest cage structure larger than $C_{60}{}^{BF}$ without abutting pentagons. Both reported that they had made a diligent,

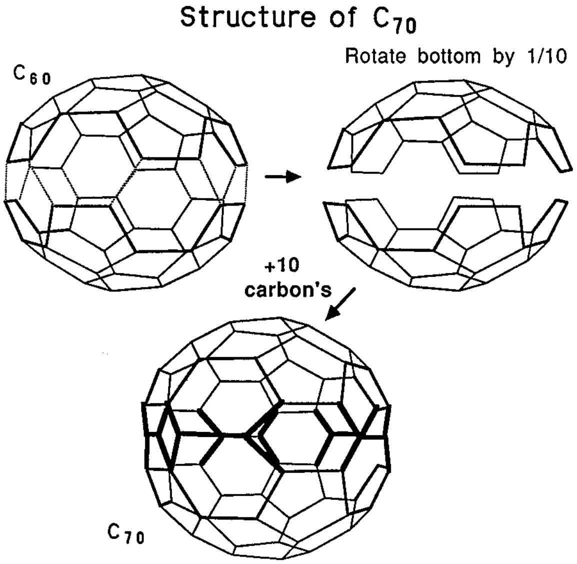

FIG. 14. Relationship of the proposed structure of C_{70} to that of C_{60} (buckminsterfullerene).

but not exhaustive, search of structures between C_{60} and C_{70} for isolated pentagon cages. Subsequently, Liu *et al.* (1991) were able to prove this conjecture. Kroto (1987) showed that the "magic number" mass spectrometer peaks containing fewer than 60 carbon atoms corresponded to structures with the minimum number of abutting pentagons. These considerations became the "isolated pentagon rule," which states that in the stable fullerenes the pentagons are isolated.

Although it was strongly supported by these theoretical considerations, the conjecture that the structure of C_{70} has D_{5h} symmetry could never be verified experimentally by molecular-beam mass spectrometry. The proof of this structure had to wait until the production of macroscopic mixtures of C_{60} and C_{70} permitted the separation of C_{60} and C_{70} (Kratschmer *et al.*, 1990) and the observation of the ^{13}C NMR spectrum of C_{70} (Taylor *et al.*, 1990).

CONJECTURE—C_{60} MIGHT BE THE CARRIER OF THE DIFFUSE INTERSTELLAR BANDS

Not all conjectures can be expected to be correct. When we wrote our initial paper on C_{60} (Kroto *et al.*, 1985) we were inspired with wildly imaginative thoughts about the potential significance of formation of this remarkable molecule in all areas of chemistry and astrophysics. Since we had been thinking of carbon-chain molecules as possible carriers of the diffuse interstellar bands (Douglas, 1977) it was natural to consider C_{60} as offering a potential explanation of the diffuse interstellar bands, and we proposed that as a possibility.

C_{60} seemed an attractive candidate for several reasons. First, any molecular carrier of the diffuse interstellar bands must be large enough so that it is not dissociated by absorbing photons of energies of up to 13.6 eV. In a large molecule such as C_{60}, when a photon is absorbed internal conversion rapidly brings the molecule back to its ground electronic state. If there is more energy available in the photon than is needed for unimolecular dissociation, then dissociation competes with vibrational reradiation of the excess energy in the infrared. With a dissociation threshold of 11 eV and so many vibrational modes, unimolecular decay even with 13.6 eV of excitation is a very slow process and loses completely to infrared reradiation. Second, there are not many diffuse interstellar bands known, and therefore any proposed carrier must give only a few bands and should not be one of a large class of equally attractive candidates. The high symmetry of C_{60} suggests only a few bands, and, while there is a fullerene family, C_{60} is often uniquely prominent. Any carrier should consist of the more cosmically abundant elements. Lastly, the diffuseness of the bands could come from mixing of the spectroscopically active excited electronic state with ground- or lower-state levels. Subsequent to our original proposal, it became obvious that C_{60} would be likely to be photoionized or to react with H atoms so that C_{60}^+ and slightly hydrogenated derivatives of C_{60} would be more attractive (Leger *et al.*, 1988; Leger *et al.*, 1990; Curl, 1993).

EXPERIMENT

Eventually, it proved possible (Haufler *et al.*, 1991) to obtain a portion of the visible electronic spectra of C_{60} and C_{70} using resonant two-photon ionization, and these spectra demonstrated conclusively that neither neutral C_{60} nor neutral C_{70} have absorptions that correspond to the known diffuse interstellar lines in the same region. These observations alone do not rule out C_{60}^+ or perhaps protonated C_{60} derivatives as carriers of the diffuse interstellar bands; however, the matrix isolation spectrum of C_{60}^+ seems to rule it out as a diffuse interstellar band carrier (Fulara *et al.*, 1993).

CONJECTURE—SOOT IS FORMED FROM SPIRALING ICOSAHEDRAL CARBON SHELLS

The control of soot formation is of enormous practical value; consequently, the nature of soot and the processes involved in its formation have been extensively studied, and this remains an active research field. Since soot consists primarily of carbon, we naturally thought about whether the chemistry involved in fullerene formation might be also applicable to soot formation. The combustion environment differs from condensing carbon vapor principally in that large quantities of hydrogen are present in combustion. Indeed, almost as many H atoms as C atoms are present in combustion soot. Combustion soot is considered to be regions of layered sheets of large polycyclic aromatic hydrocarbons joined by disorganized regions.

It seemed to us that the fullerenes were forming in a process where small carbon clusters such as C_2 and C_3 were adding to a growing, curving sheet of five- and six-membered rings. Curvature and ultimate closure into

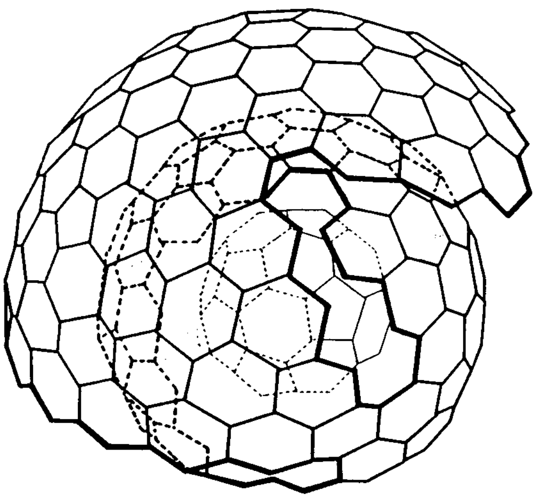

FIG. 15. Spiraling icosahedral shell model of a growing soot particle. It has almost completed its second shell of growth.

fullerenes was brought about by some sort of ring rearrangement process that let the carbon cluster find its lowest-energy, least reactive forms. The growth of polycyclic hydrocarbons in soot formation was thought to be by the creation of a reactive carbon atom on the periphery by H atom abstraction from a peripheral CH bond followed by acetylene addition to the reactive center, followed by ring closure with H atom elimination (Frenklach *et al.*, 1984). The similarity between the process we imagined for fullerene formation and the polycyclic hydrocarbon growth process in combustion soot formation seemed striking to us. The main difference seemed likely to be that hydrogen on the edges might interfere with the fullerene closure processes leading to imperfect cages. Perhaps a soot particle was the result of such imperfect growth and would resemble a spiraling fullerenic shell. Thus we proposed that a soot particle would be based upon a spiraling icosahedral shell similar to the structure shown in Fig. 15.

EXPERIMENT

This suggestion was met with disfavor by some members of the soot community (Frenklach and Ebert, 1988; Baum, 1990; Ebert, 1990). However, it did result in searches for fullerenes in flames by some of the leading combustion and soot scientists. Thus Homann found C_{50}^+, C_{60}^+, and C_{70}^+ prominently in hydrocarbon flames (Gerhardt *et al.*, 1987). He suggested that soot particles might be supports for fullerene growth (Gerhardt *et al.*, 1989). More recently he has proposed more elaborate and detailed models for fullerene formation (Baum *et al.*, 1991) and its relation to soot (Baum *et al.*, 1992). After C_{60} and C_{70} became available in bulk, soot scientists began looking for these species in combustion soots with success (Howard *et al.*, 1991; McKinnon *et al.*, 1992). Under optimal conditions the yield of C_{60} plus C_{70} was as much as 20% of the soot and up to 0.5% of the carbon fed (Howard *et al.*, 1992) making flames a practical preparation scheme for fullerenes. Quite recently, electron microscope examination of nanostructures in flame soots has revealed the whole range of fullerenic structures: fullerenes, nanotubes, and the nested fullerenes resembling Russian dolls (Chowdhury *et al.*, 1996). These observations are strong evidence that carbon has a strong propensity to form these structures in chemically quite different environments where elemental carbon forms are produced.

Thus some very special chemistry does not appear to be needed for fullerene formation. Howard has proposed a detailed kinetic scheme for the formation of C_{60} and C_{70} in flames (Pope *et al.*, 1993) which parallels the standard mechanism for the formation of polyaromatic hydrocarbons, which are considered to be the soot precursors. Nevertheless, fullerene formation and soot formation remain to him clearly distinct processes.

The soot community remains united in the belief that, while soot might produce fullerenes as an offshoot, soot formation is a different process from fullerene formation and that soot is primarily composed of polycyclic hydrocarbons and that there is no evidence for spiraling icosahedral shells. It should be noted that it is known that more than half of the soluble polycyclic hydrocarbon inventory of flames contain five-membered rings and therefore curvature (Lam *et al.*, 1991). Whether the curvature introduced by such five-membered rings plays any role in the formation of soot particles remains an interesting open question.

CONCLUSION

In science, conjecture drives both experiment and theory for it is only by forming conjectures (hypotheses) that we can make the direction of our experiments and theories informed. If such and such is true, then I should be able to do this experiment and look for this particular result or I should be able to find this theoretical formulation. Conversely, experiment and theory drive conjecture. One makes a startling observation or has a sudden insight and begins to speculate on its significance and implications and to draw possible conclusions (conjecture).

However, not all conjectures are equally valid or useful. Thus the conjecture that C_{60} might be related to the diffuse interstellar bands was and remains wildly speculative. It has been one of my favorite speculations (Curl, 1993) because it has many things going for it: carbon is injected into the medium and C_{60} forms spontaneously in condensing carbon under the right conditions, C_{60} is unique and its compounds are limited in number and only a few species should be involved in the diffuse interstellar bands, C_{60}^+ could survive the UV present in the interstellar medium, the diffuseness of the bands could come from mixing of the spectroscopically active excited electronic state with ground- or lower-state levels. However, conjectures should be judged by the accumulation of evidence that supports and contradicts them. To date, there has been plentiful contradictory evidence for the C_{60} connection to the diffuse interstellar bands and no supporting evidence. Primarily, this conjecture has the fatal defect that it has stimulated little productive science.

The conjecture that soot may consist of spiraling spheroidal shells of carbon belongs in a slightly different category. It was based upon a hypothesis, which was somewhat vague at the time, about how fullerenes may form. Thus it was not a wild idea in that there was some support for the speculation. In my opinion, the conjecture that soot consists of spiraling spheroidal shells is probably wrong. However, I think it likely that there is some more subtle connection between the curvature introduced by five-membered rings and soot formation. Regardless of its validity, this conjecture has turned out to be extremely valuable, because it got the soot community, in some cases somewhat grumpily, thinking about the formation of fullerenes and other carbon morphologies in flames. As a result, fullerenes were found in flames and soot. It appears that all the new carbon morphologies can be produced in flames (Chowdhury *et al.*, 1996).

Turning to the central theme, the conjecture of Jones (1966) that carbon cage compounds might have interesting properties, and the conjecture of Osawa (1970) and several others that C_{60} would be a stable, chemically interesting molecule are examples of conjectures that are correct and valuable, but which by themselves cannot be made useful. There was no way, or no easy way (remember Chapman), to proceed to further work based on the conjecture.

On the other hand, the conjecture that a new whole class of carbon-cage compounds, the fullerenes, are formed spontaneously in condensing carbon vapor has led to sweeping consequences. At the time, this hypothesis seemed to be the only logical explanation of the observed carbon mass-spectra distributions, but it was not self-evident. As we have seen, we tested this conjecture in a variety of experiments, which always provided evidence supporting the conjecture. This pattern of repeated confirmation of expected consequences is what is expected for a correct hypothesis. In the long run, the fullerene hypothesis has proved to be spectacularly correct and it has provided the basis for whole new branch of organic chemistry.

Finally, I believe that the conjecture that started it all, namely that truncated icosahedron C_{60} forms spontaneously in condensing carbon, scarcely belongs in the category of conjecture. The three mass spectra in Fig. 5 when coupled with the conditions under which they were obtained demand that the species responsible for the prominent peak at C_{60} must be singularly different and chemically relatively unreactive. The human mind can conceive of no other isomer of C_{60} that better fits this requirement.

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