

# DAWN OF THE FULLERENES: EXPERIMENT AND CONJECTURE

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by

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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<sup>1</sup> 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 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.<sup>2</sup>

Apparently the first person to imagine the truncated icosahedron isomer of  $C_{60}$  shown in Fig. 1 was Osawa.<sup>3,4</sup> Osawa conceived of the  $C_{60}$  structure while meditating on the structure of corannulene ( $C_{20}H_{10}$ ), which has a cent-

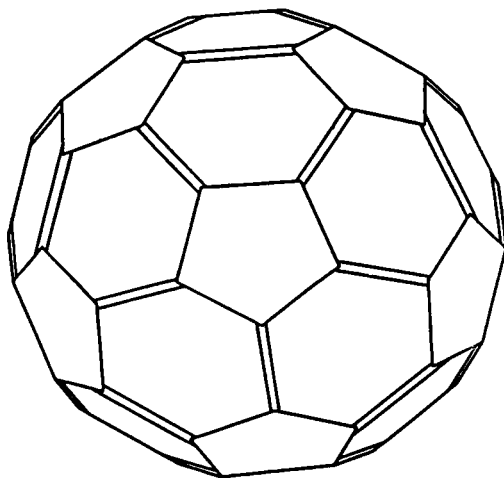


Fig. 1. Truncated icosahedron  $C_{60}$  with dominant Kekulé structure.

ral 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,<sup>5</sup> and repeated<sup>6</sup> independently some years later in the USA as part of a larger article. The Hückel calculation was repeated again by Haymet<sup>7</sup> in his discussion of the stability of the molecule.

The synthetic organic chemist, Orville Chapman, took the challenge of the synthesis of truncated icosahedron  $C_{60}$  seriously in the early 1980's, obtained funding from the National Science Foundation for this purpose, and set to work with several graduate students on its total synthesis.<sup>8</sup> 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<sup>9,10</sup> by radioastronomy in the interstellar medium 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<sup>11</sup> that electronic absorptions of long-chain carbon molecules,  $C_n$  ( $n=5-15$ ), are the source of the diffuse interstellar bands.<sup>12</sup> The work on formation of carbon chain compounds was ultimately published,<sup>13,14</sup> 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<sup>15</sup> that truncated icosahedron  $C_{60}$  (buckminsterfullerene) is formed spontaneously in condensing carbon vapor. Accounts of this have been given<sup>16,17</sup> by two of the five people involved and in two books on the discovery of the fullerenes.<sup>8,18</sup> 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.

However, in order to understand what we did it is necessary to learn something about the apparatus<sup>19-21</sup> invented by Richard Smalley 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,<sup>20-23</sup> copper trimer,<sup>24</sup> and  $SiC_2$ .<sup>25</sup> 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. Fig. 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 nsec 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.

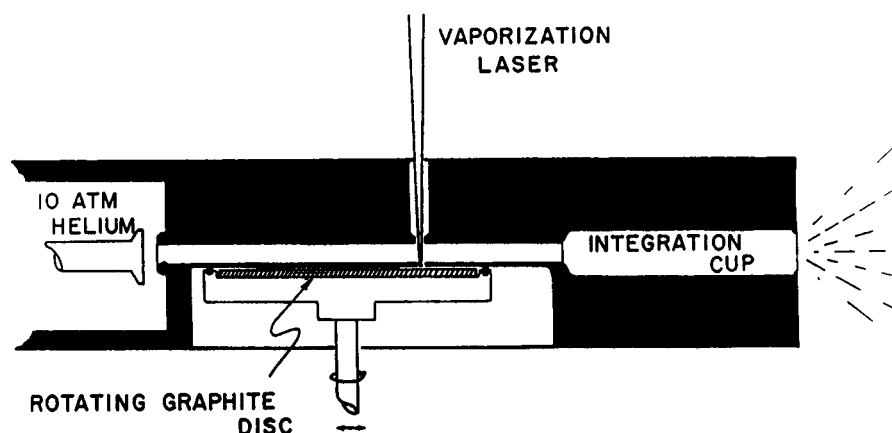


Fig. 2. Laser vaporization source for producing molecular beams of clusters of refractory materials. The integrating cup can be removed. For the carbon experiments, the target is a graphite disk which is rotated slowly to provide fresh vaporization surface. The vaporization laser, a 5 nsec pulse at 532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

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 K. 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 nsec). 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

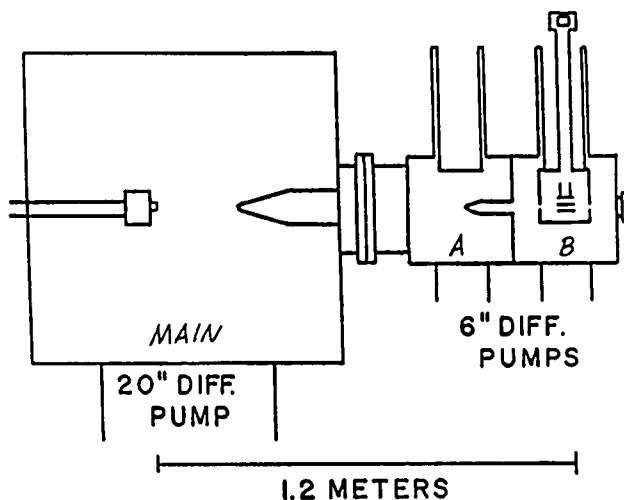


Fig. 3. Molecular beam photoionization time-of-flight mass spectrometer.

mass reach a final velocity which is less than ions of lesser mass. Therefore, the mass of the ion in 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 2. Fig. 4 shows a cluster distribution for carbon similar to that obtained previously by Rohlfling, Cox and Kaldor<sup>26</sup> in a essentially the same apparatus. In Rohlfling, 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 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<sup>15</sup> 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. 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

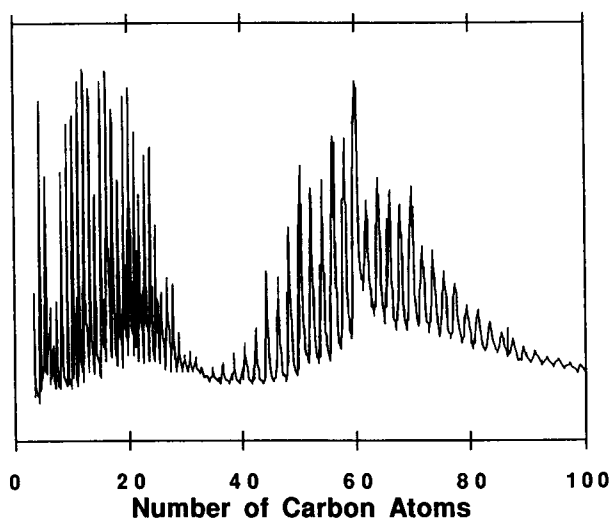


Fig. 4. Carbon cluster distribution observed under mild clustering conditions. This distribution is similar to that obtained by Rohlfling, Cox, and Kaldor.<sup>26</sup>

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.

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

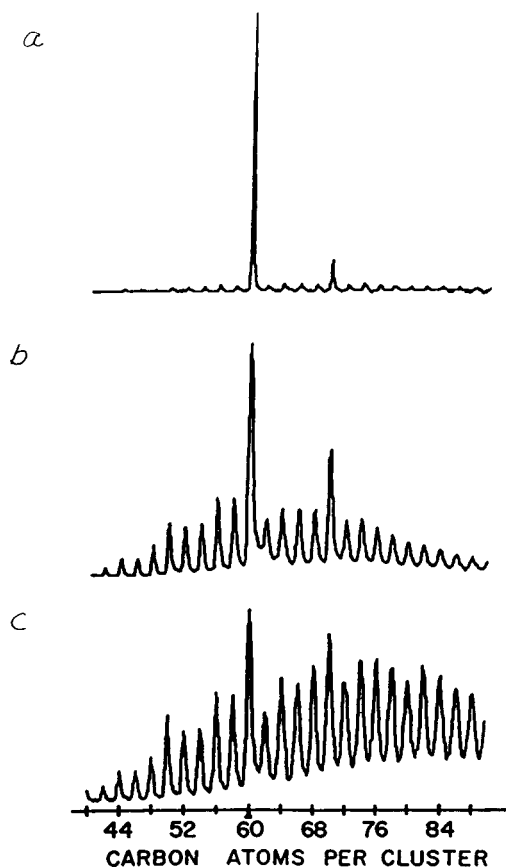


Fig. 5. Mass spectrum of the  $C_{60}$  mass region showing  $C_{60}$  growing prominent. Panel c corresponds to a situation where the helium backing pressure is low and there is no integration cup. Panel b was obtained with full helium backing pressure with vaporization in the center of the gas pulse,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

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. Fig. 6 "control" shows a distribution intermediate between Rohlfling, Cox and Kaldor and those observed with nearly equal intensity odd clusters. Thus even in the bottom panel of Fig. 5 the observation of only clusters with 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. 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 only be explained 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<sup>27</sup> which demonstrated a similar prominence of  $C_{60}^+$  upon photoionization with a 7.9 eV  $F_2$  excimer laser.

The truncated icosahedron form of  $C_{60}$  is clearly a special structure which 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 12,500 possible Kekulé structures<sup>28</sup> (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 counter-intuitive 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.

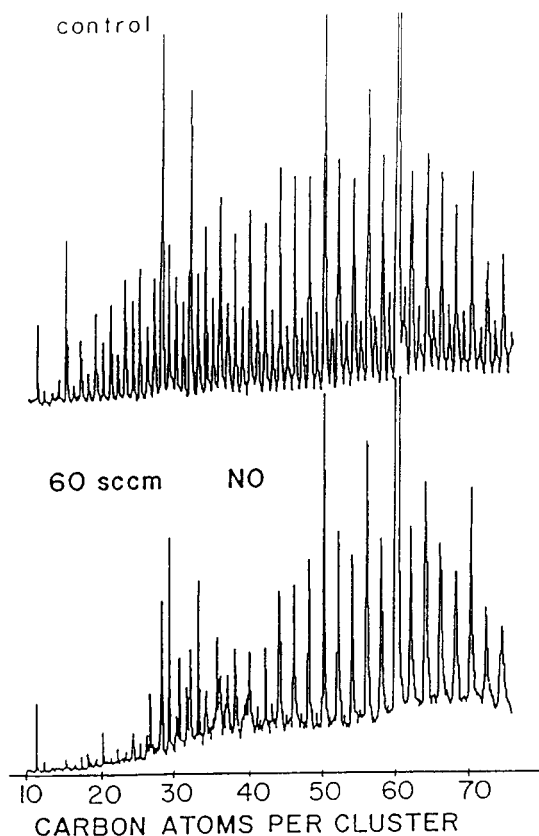


Fig. 6. Reaction of carbon clusters with NO. The upper control mass spectrum was obtained without added NO. In the lower spectrum roughly 1 Torr of NO was added to the gas stream in the fast-flow reaction tube. It is clear that the odd clusters react with NO. The various products of these reactions are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

In science, more proof is always demanded. Later experiments<sup>27,29</sup> 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<sup>7</sup> of Euler's rule<sup>30</sup> 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 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.<sup>31,32</sup> 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.<sup>33</sup> 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 were carried out on the carbon cluster ions hypothesized to be fullerenes using a tandem time-of-flight mass spectrometer.<sup>34</sup> The apparatus is shown in Fig. 7. In these experiments,

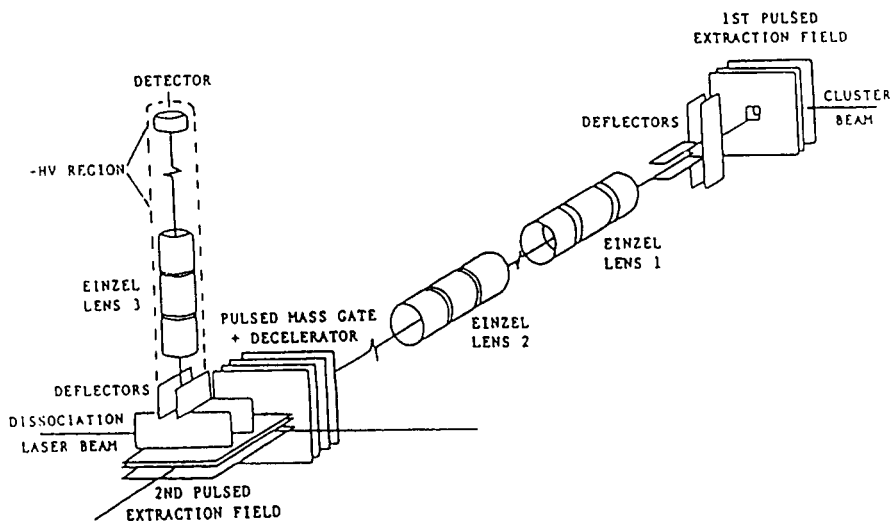


Fig. 7. Tandem time-of-flight mass spectrometer. The molecular beam containing residual ions from the vaporization plasma enters the extraction region of the primary mass spectrometer where a 2000 V pulse is applied across the grids. The deflectors remove the molecular beam velocity. The einzel lenses 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.

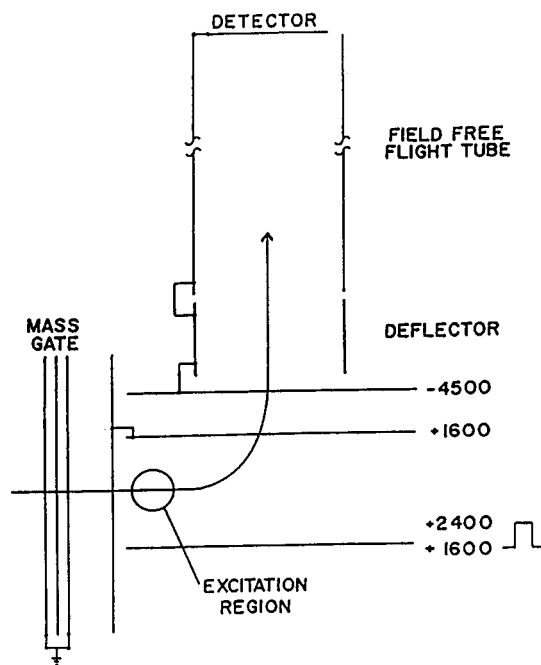


Fig. 8. Detail of the photofragmentation region of the tandem TOF apparatus showing the mass gate, laser excitation region, extraction optics and flight tube.

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,<sup>35</sup> 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.<sup>36</sup> For example, there are<sup>37,38</sup> 1812 fullerene isomers (i.e. cages containing 12 pentagons and 20 hexagons) of  $C_{60}$  alone. 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  $C_{60}$ ,  $C_{60}^{BF}$ .

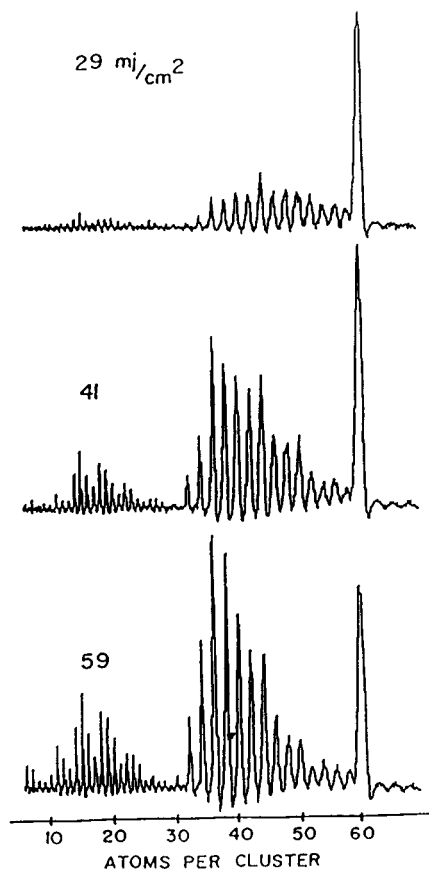


Fig. 9. Photofragmentation pattern of  $C_{60}^+$  showing loss of even number of carbon atoms and break off at  $C_{32}^+$ .

When these energies are combined with the bond dissociation energy of  $C_2^{39}$  of 6.21 eV, the overall energy change in fragmentation can be calculated. Thus the overall energy change in



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



$\Delta E = 11.2$  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  $\mu\text{sec}$  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  $C_{60}$  would be apparent in the fragmentation pattern. Fig. 11 shows fragmentation of some larger clusters when the sample is irradiated just before the acceleration region of the second TOF as shown in Fig. 9. Only a few  $\mu\text{sec}$  are available for fragmentation after irradiation and

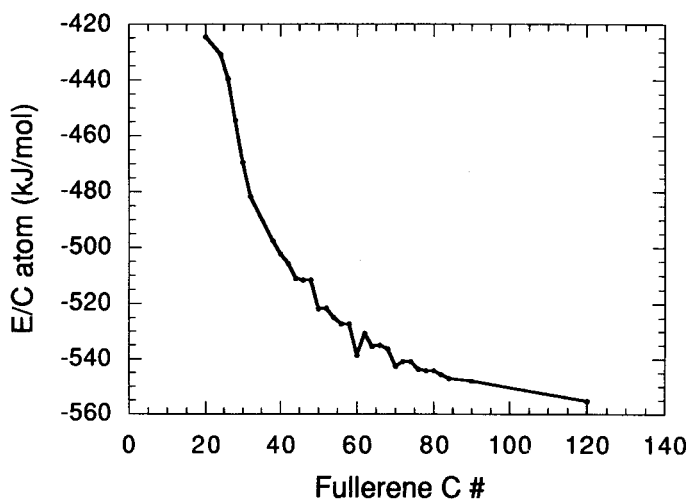


Fig. 10. Energy per carbon atom relative to atomic C as a function of fullerene cluster size at the STO-3G/SCF level at the MM3 optimized geometry for the lowest energy fullerene structure for each size. This figure is based upon the calculations of R. L. Murry, D. L. Strout, and G. E. Scuseria.<sup>35</sup>

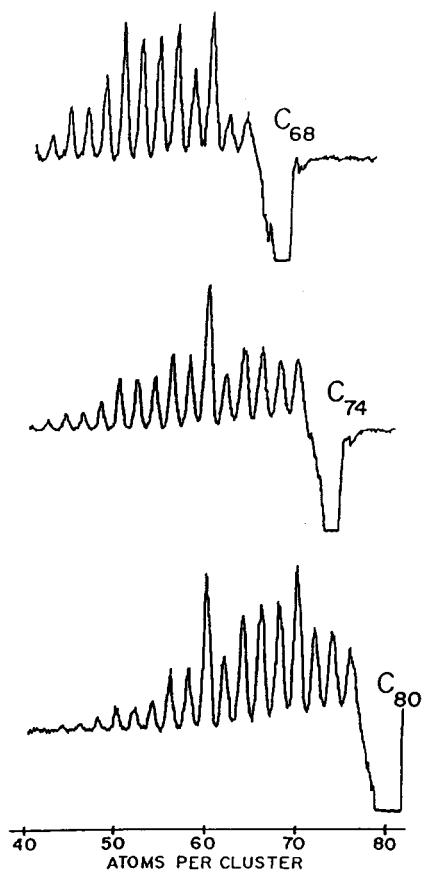


Fig. 11. ArF ( $15 \text{ mJ cm}^{-2}$ ) fragmented large even carbon clusters. There is no difference in the fragmentation pattern of the large clusters.  $C_{60}$  and  $C_{70}$  are slightly favored.

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* TOF extraction region just before extraction and the ions which 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  $\mu\text{sec}$ .

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

Assume that a fragmentation which 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  $C_{60}^{\text{BF}}$  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.

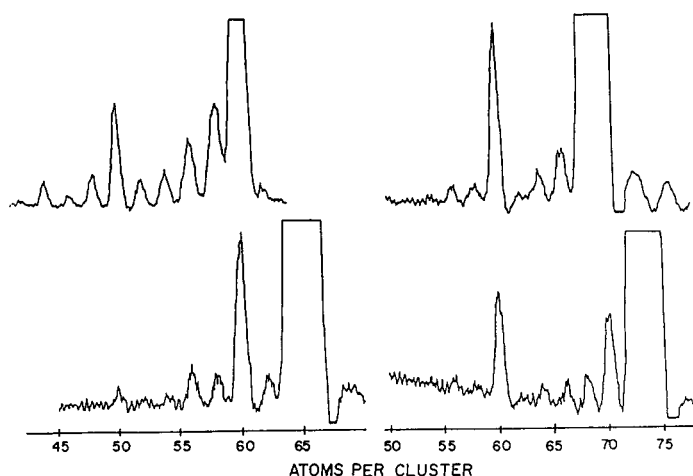


Fig. 12. Metastable TOF mass spectra for 60, 66, 70, and 74 atom clusters. The clusters were irradiated 1  $\mu\text{sec}$  before the first extraction pulse with  $15 \text{ mJ cm}^{-2}$  ArF. The ions were mass gated at the time appropriate to the parent ions listed above and analyzed in the second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

Figs. 9, 11, and 12 taken together provide striking evidence that 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 break-off 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.

### EXPERIMENT – ENDOHEDRAL METALLOFULLERENES AND “SHRINK WRAPPING”

Success in forming adducts with a single lanthanum atom was almost immediately achieved.<sup>40</sup> 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 were carried out<sup>41</sup> 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  $C_2$ ,  $C_4$ ,  $C_6$  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

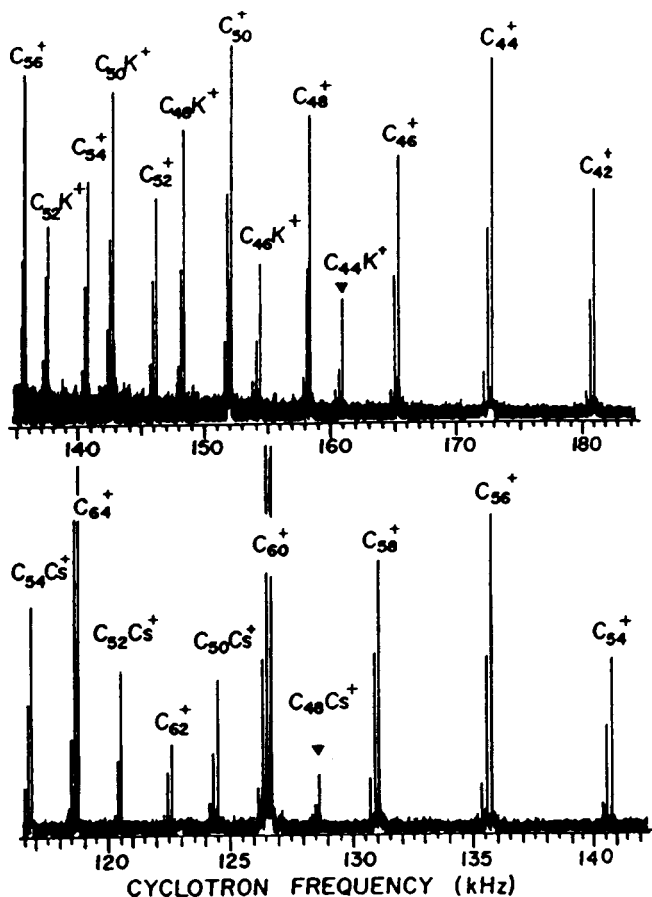


Fig. 13. The low mass portion of the fragment ions produced by intense laser excitation of  $C_{60}K^+$  (panel A) and  $C_{60}Cs^+$  (panel B) in the FT-ICR trap. The clusters containing carbon only seen in these spectra arise from fragmentation of empty fullerene ions simultaneously trapped with the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

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. Fig. 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.

#### 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<sup>40</sup> one in which a

band of five hexagons was added around the equator of  $C_{60}$ . 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<sup>7</sup> that such connected rings would be destabilizing. Shortly thereafter, Schmalz *et al.*<sup>42</sup> 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<sup>43</sup> and Schmalz *et al.*<sup>44</sup> 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, but not exhaustive, search of structures between  $C_{60}$  and  $C_{70}$  for isolated pentagon cages. Subsequently, Liu *et al.* were able to prove<sup>45</sup> this conjecture. Kroto<sup>43</sup> 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<sup>46</sup> of macroscopic mixtures of  $C_{60}$  and  $C_{70}$  permitted the separation of  $C_{60}$  and  $C_{70}$  and the observation of the  $^{13}C$  NMR spectrum of  $C_{70}$ .<sup>47</sup>

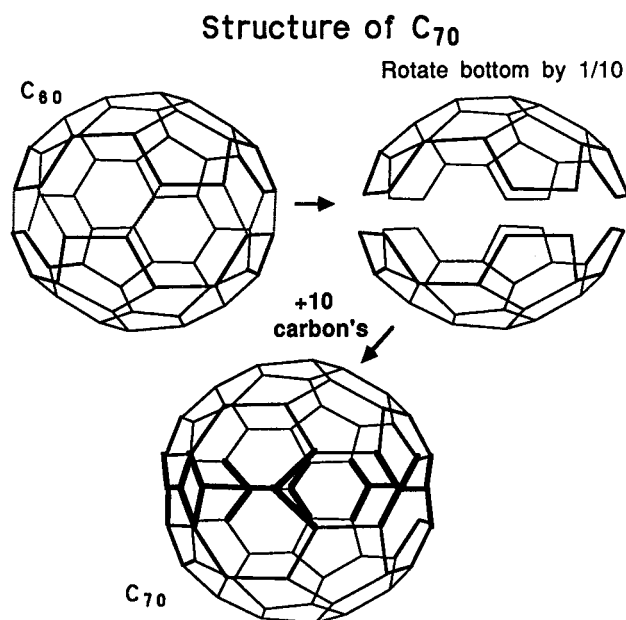


Fig. 14. Relationship of the proposed structure of  $C_{70}$  to that of  $C_{60}$  (buckminsterfullerene).



### CONJECTURE – C<sub>60</sub> MIGHT BE THE CARRIER OF THE DIFFUSE INTERSTELLAR BANDS

Not all conjectures can be expected to be correct. When we wrote our initial paper<sup>15</sup> on C<sub>60</sub>, 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 (dib's),<sup>11</sup> it was natural to consider C<sub>60</sub> as offering a potential explanation of the diffuse interstellar bands, and we proposed that as a possibility.

C<sub>60</sub> seemed an attractive candidate for several reasons. First, any molecular carrier of the dib's 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<sub>60</sub>, 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 dib's 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<sub>60</sub> suggests only a few bands, and, while there is a fullerene family, C<sub>60</sub> 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<sub>60</sub> would be likely to be photoionized or to react with H atoms so that C<sub>60</sub><sup>+</sup> and slightly hydrogenated derivatives of C<sub>60</sub> would be more attractive.<sup>48-50</sup>

Eventually, it proved possible<sup>51</sup> to obtain a portion of the visible electronic spectra of C<sub>60</sub> and C<sub>70</sub> using resonant two-photon ionization, and these spectra demonstrated conclusively that neither neutral C<sub>60</sub> nor neutral C<sub>70</sub> have absorptions that correspond to the known diffuse interstellar lines in the same region. These observations alone do not rule out C<sub>60</sub><sup>+</sup> or perhaps protonated C<sub>60</sub> derivatives as carriers of the diffuse interstellar bands; however, the matrix isolation spectrum of C<sub>60</sub><sup>+</sup> seems to rule it out<sup>52</sup> as a diffuse interstellar band carrier.

### 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 principally differs from condensing carbon vapor 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 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 (PAH) in soot formation was thought<sup>53</sup> 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. The similarity between the process we imagined for fullerene formation and the PAH 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 fullerene shell. Thus we proposed that a soot particle would be based upon a spiraling icosahedral shell similar to the structure shown in Fig. 15.

This suggestion was met with disfavor by some members of the soot community.<sup>54-56</sup> However, it did result in searches for fullerenes in flames by some of the leading combustion and soot scientists. Thus Homann<sup>57</sup> found  $C_{50}^+$ ,  $C_{60}^+$ , and  $C_{70}^+$  prominently in hydrocarbon flames. He suggested<sup>58</sup> that soot particles might be supports for fullerene growth. More recently he has proposed more elaborate and detailed models for fullerene formation<sup>59</sup> and

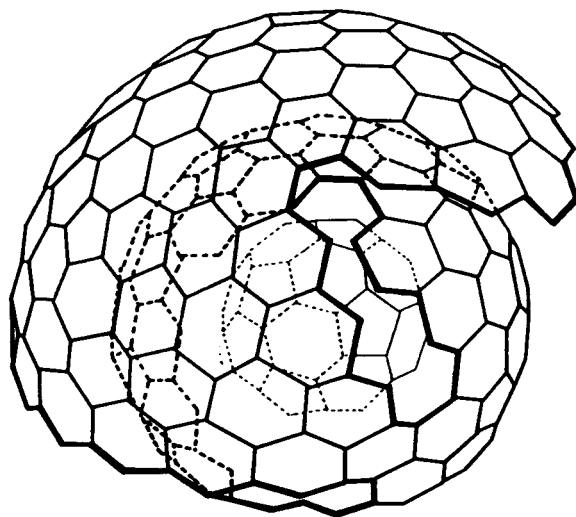


Fig. 15. Spiraling icosahedral shell model of a growing soot particle. It has almost completed its second shell of growth.

its relation to soot.<sup>60</sup> After  $C_{60}$  and  $C_{70}$  became available in bulk, soot scientists began looking for these species in combustion soots with success.<sup>61,62</sup> 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,<sup>63</sup> making flames a practical preparation scheme for fullerenes. Quite recently, electron microscope examination<sup>64</sup> of nanostructures in flame soots has revealed the whole range of fullerene structures: fullerenes, nanotubes, and the nested fullerenes resembling Russian dolls. 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<sup>65</sup> a detailed kinetic scheme for the formation of  $C_{60}$  and  $C_{70}$  in flames 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 PAH's and that there is no evidence for spiraling icosahedral shells. It should be noted that it is known<sup>66</sup> that more than half of the soluble PAH inventory of flames contain five-membered rings and therefore curvature. 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,<sup>50</sup> 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<sup>64</sup> that all the new carbon morphologies can be produced in flames.

Turning to the central theme, the conjecture of Jones<sup>1,2</sup> that carbon cage compounds might have interesting properties, and the conjecture of Osawa<sup>3</sup> and several others that  $C_{60}$  would be a stable, chemically interesting molecule are examples of conjectures which 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 a 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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