

A Postbuckminsterfullerene View of Carbon in the Galaxy

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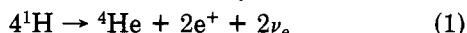
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The molecule C_{60} , buckminsterfullerene, was discovered¹⁻³ during laboratory experiments motivated by problems associated with processes involving carbon in stars and space.^{4,5} Astronomical puzzles also lay behind the experiments which led to the molecule's extraction and structure confirmation.⁶⁻⁸ In particular, as radioastronomy allowed us to pry ever deeper into the chemical mysteries of the interstellar medium (ISM), it became clear that there was some chemical relationship between carbon chain synthesis and the way in which carbon/graphite dust forms in space (and perhaps soot forms on earth).^{4,5} The experiments aimed at probing these relationships uncovered the existence of C_{60} and highlighted the fact that it might be involved in some intimate and as yet unspecified way in the general carbon nucleation process. Although the resulting breakthrough (the birth of fullerene chemistry) has opened up exciting new avenues of chemistry, physics, and materials science here on earth,⁹ the original astrophysical questions still remain and are even more tantalizing now than they were before. Some of the puzzles are here readdressed in the light of the new understanding which the fullerene discovery has brought. Indeed we shall look at the questions through magenta colored spectacles and note that there are new and even more intriguing parallels between the behavior of carbon on earth and in space. This article contains a brief account of the processes responsible for the synthesis of carbon in stars and its dissemination throughout the galaxy as this information is deemed necessary to gain an intrinsic understanding of the amazing role carbon plays in nature.

The Nucleosynthesis of Carbon in Stars

It has long been realized that we owe our existence to the uniquely idiosyncratic chemical properties of carbon. It has also been recognized that the existence of significant amounts of the element carbon in the universe was due to a peculiar set of fortuitous coincidences in the elemental nuclear reaction scheme.¹⁰⁻¹² The basic evolutionary process which occurs in stars, such as the sun, involves the fusion of hydrogen into helium, an exothermic reaction (ν_e , neutrino):



A star will shine by this process—in the case of the sun, for some 10^{10} years—before the hydrogen supply

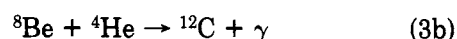
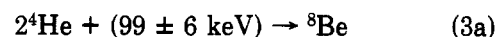
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Harry Kroto was born in Wisbech, Cambridgeshire, England, in 1939. He gained a B.Sc. in 1961 and Ph.D. in 1964 at the University of Sheffield. After postdoctoral fellowships at NRC, Ottawa, Canada (1964-1966), and Bell Telephone Laboratories, Murray Hill, NJ (1966-1967), he went to the University of Sussex, where he is now a Royal Society Professor. Apart from research interests in spectroscopy, interstellar molecules, unstable intermediates, carbon molecules, and materials, his main interest is in graphic art and design.

starts to run out, cutting off the gas which supports the star against gravitational collapse. (Note that radiation pressure is also important in higher mass stars.) Before this reaction peters out completely, pressures and temperatures rise and a second process ignites in the core:



This step¹² is a three-body reaction and should be very slow, so it was conjectured that it might take place in two stages:



It was suggested that the first step might be autocatalytic since ^8Be is metastable with a lifetime of ca. 10^{-16} s compared with a He-He collision time of ca. 10^{-21} s. Furthermore, Hoyle reasoned, from the incontrovertible evidence that there is a significant quantity of carbon in the galaxy, the biosphere, and of course, people, that there must be two other fortuitous factors. The most important was that reaction 3b must be resonant, i.e., the energy of $^8\text{Be} + ^4\text{He}$ (ca. 7.7 MeV) must be almost the same as, or slightly below, that of an excited state of ^{12}C . Otherwise essentially no carbon could form in this way. This piece of "anthropic" inspiration—the first time a nuclear level energy had ever been predicted—turned out to be quite correct. Hoyle furthermore reasoned that the energy of ^{16}O must lie below that of $^{12}\text{C} + ^4\text{He}$ and be nonresonant or else any carbon produced by the triple- α mechanism would be processed efficiently into oxygen. Some have seen divine intervention as having tampered with these apparently "random" numbers.

Carbon in the Interstellar Medium

Fifteen thousand million years ago the Universe was born with a bang—or so those who listen for the re-

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verberations tell us—and it appears to have been expanding ever since. It has been estimated that within the first second the Universe cooled to 10^{10} K and when the temperature had dropped to 10^9 K, nucleosynthesis was feasible and hydrogen fused to helium. After about 3 min the Universe consisted mainly of H (76% by mass) and He (24%) and expansion and cooling had made further nucleosynthesis no longer feasible. As time evolved, inhomogeneities occurred and the gas broke up into localized condensations driven first by differential radiation pressure and then by self-gravity. Galaxy-sized objects (ca. $10^{11}M_{\odot}$ mass) formed which ultimately developed further subcondensations (of mass $(0.2\text{--}50)M_{\odot}$): the stars. Many stars have masses similar to that of the Sun (M_{\odot}). Process 1 is the primary energy source for all stars, and most of the life of a star is spent converting H to He.¹³

The way in which a star evolves depends critically on its mass. Eventually a core of He forms at the center of the star surrounded by a shell of burning H. In the case of a $<0.5M_{\odot}$ star, the H will eventually be consumed and the energy released will no longer prevent gravitational collapse. The star loses much of its hydrogen and contracts to form a small hot, dense white dwarf. Typically these objects have surface temperatures of ca. 20000 K compared to the Sun's temperature of 6000 K. No further reactions can occur, and white dwarfs cool to end up ultimately in the stellar graveyard as cold black dwarfs.¹³ More massive stars ($M < 8M_{\odot}$) expand to form red giants in which the He in the core can fuse to form C, O, and higher elements;¹⁴ they then settle down as hot smaller stars. The outer gaseous envelope expands again as the star passes through a second red-giant phase as the He burning slows down. The combination of a very hot core and large expanded envelope makes such stars very luminous even though they are relatively cool (surface temperatures typically 3000 K). This stage of the star's evolution lasts about 10^8 years.¹⁴

For $>8M_{\odot}$ stars, further reactions can occur forming many shells of elements around the core. Finally, when iron (the most stable element) forms, no further fusion can take place and the star collapses catastrophically. The resultant explosion is termed a supernova. Elements heavier than iron are synthesized in such high neutron flux events and blown into the ISM. More common outbursts are novae associated with the complicated dynamics of binary star evolution. These less catastrophic events are also important sources of interstellar carbon. More typical, and particularly important for our purposes, are stars with masses $<8M_{\odot}$ in their red-giant phase. Here the He core (containing elements such as C, N, and O) collapses, but is unable to reach the conditions where further nuclear reactions can occur. As the core contracts, a hot white dwarf ($T = 6000\text{--}30\,000$ K) rich in carbon and oxygen forms. The star still has burning hydrogen and helium shells, which cause considerable convection in the red-giant envelope which remains. This convective envelope becomes very unstable and dredges up processed material to the stellar surface. Stars of this type are classified by their spectra. The C/O ratio is important for our discussion: If this ratio is <1 , the star is said to be "oxygen rich"

and most of the carbon expelled by the star is thought to be locked up in CO gas. If this ratio is >1 , the star is said to be "carbon rich" and much of the excess carbon (over O) is believed to be locked up (mainly) in carbon (graphite?!) grains.

The instability in the envelope causes shock waves which transport matter to large distances beyond the stellar surface. This material eventually cools, and in the case of carbon stars, carbon molecules and dust condense out. Radiation pressure propels the molecule/dust envelope out into the general ISM. Scattering by dust often obscures the star from optical view. Such mass-losing red giants¹⁵ are, however, very bright in the IR region. The fascinating red giant IRC+10216 (see below) discovered by Becklin et al.¹⁶ is exceptionally bright in the IR region. Eventually the shell is blown away, completely exposing the hot central star. Starlight ionizes the shell, causing it to emit in the visible and UV regions as well as the IR region. This later evolutionary phase is visible optically, and the resulting object is called a planetary nebula. The transition from red giant to planetary nebula is believed to be very quick: less than 10^4 years. Such objects often seem to expel material in two distinct lobes, and such bipolar outflows disperse material into the ISM, eventually leaving behind a solitary white dwarf.

Thus stars enrich the ISM with atoms, molecules, and dust which eventually reaggregate to form the molecular clouds and ultimately new generations of stars. The main sources of carbon in the ISM are red giants and supergiant stars, contributing some 50% of the carbon in the galaxy. Novae and supernovae are also important sources whereas planetary nebulas appear to contribute an order of magnitude less. Jura has discussed carbon-rich objects.^{15,17}

Chemical Composition of the Carbonaceous Component of the Cosmos

Many molecules have now been detected in the ISM and stars.^{18,19} Indeed the first molecules identified in the ISM—CH, CH⁺, and CN—all contain carbon. Although these species were discovered between 1936 and 1941, it was not until the breakthrough in 1968 when Townes and co-workers used radio techniques to detect ammonia²⁰ that a detailed understanding of the chemistry of the ISM was possible. Soon after this advance, HCN was observed by Snyder and Buhl,²¹ and then HC₃N was detected by Turner.²² The more complicated molecules were less common, and from relative abundance comparisons and intuition was developed a rough "rule of thumb": A molecule with a particular number of heavy atoms (C, O, or N) was, in general, less abundant by a factor of ca. 10 than one with one less heavy atom.

At about the same time, elegant theories of interstellar molecule formation were being developed in-

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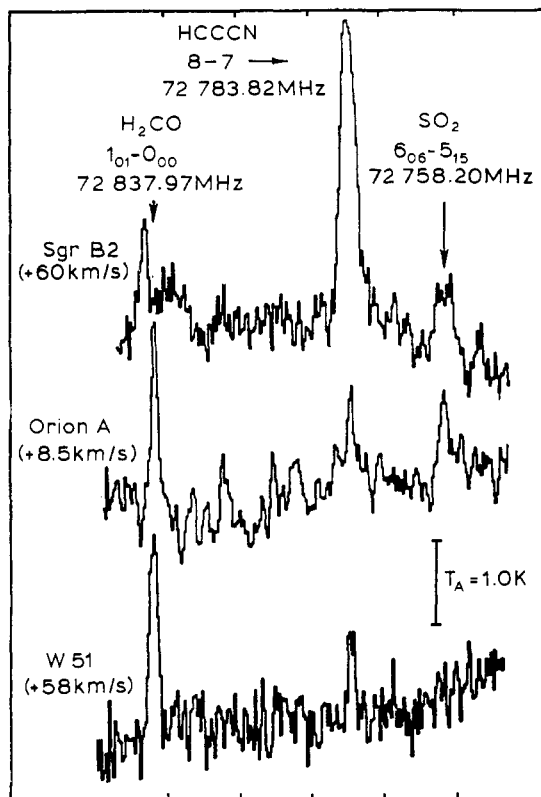


Figure 1. Radio lines²⁷ suggesting that the cyano polyne abundance in Orion is significantly lower than that in Sagittarius. Reprinted with permission from ref 18. Copyright 1981 Butterworths.

volving gas-phase ion-molecule processes and grain surface catalysis. The ion-molecule scenarios of Herbst and Klemperer²³ as well as Dalgarno and Black²⁴ were particularly effective in explaining much of what had been learned in the late 1960s and early 1970s and neatly accounted for ions and radicals which had been discovered,^{18,19} in particular, fascinating ionic species such as HCO^+ (protonated CO), which Klemperer assigned to a strong unidentified radio line.²⁵ In general the spectroscopic information which enabled the interstellar assignments to be made came from the vast catalog of microwave data which had been built up since the war, when microwave oscillators were developed. Microwave spectroscopy techniques, however, were also being developed; it was becoming possible to detect new "unstable" molecules in the laboratory, and sometimes such detections were a prelude to their detection in space. In 1975 the first cyano polyne, HC_5N , was synthesized,²⁶ which had two C atoms more than HC_3N . Stimulated by the HCN ²¹ and HC_3N ²² detections, a radio search for HC_5N , using the NRC telescope in Algonquin Park, was initiated. In Figure 1 is shown a comparison of the signals for HC_3N as observed from various clouds²⁷ showing that the giant molecular cloud complex in SgrB2 near the galactic center is a promising site to search for HC_5N whereas Orion, which had been and still is a very happy hunting ground for most in-

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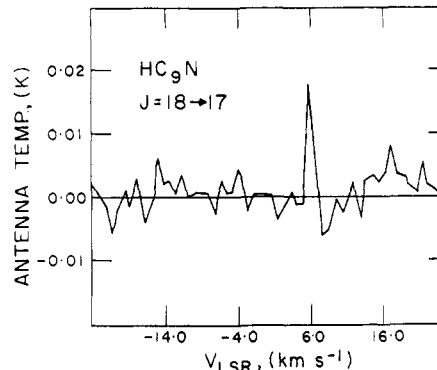


Figure 2. Radio line of HC_9N detected in a molecular cloud in Taurus. Reprinted with permission from ref 32. Copyright 1978 University of Chicago Press, Journals Division.

terstellar molecules, was much less promising. It should be noted that at the time the search for HC_5N seemed like a very long shot because the above "rule of thumb" suggested that HC_5N should be some 10-100 times less abundant than HC_3N . In the event it turned out that HC_5N was readily detectable;²⁸ it was much more abundant than expected! This surprising discovery stimulated the laboratory synthesis²⁹ of the next species, with two more C atoms (HC_7N), and it too was detected.³⁰ From a series of laboratory frequency measurements on the species HC_nN ($n = 1, 3, 5,$ and 7), Oka³¹ was able to predict the radio frequency of the next member, HC_9N , and this too was detected by radioastronomy³² (Figure 2). A particularly good place to detect the chains turned out to be a tiny dense black cloud known as TMC1 (Taurus Molecular Cloud 1), which seemed to be chock-a-block with carbon molecules.

One of the most fascinating objects is the star R Cor Borealis (and other members of this family of extremely hydrogen-poor carbon-rich stars, called RCorBor stars). These stars have very low H content (H/C ca. 10^{-5})³³ and are variable. RCorBor itself is very luminous and is usually at maximum light; however, the luminosity occasionally fades by 6-9 magnitudes ($1 \text{ mag} \equiv 100^{1/5}$) for periods lasting several weeks.³³ The periodicity is very irregular, varying between 1 and 10 years. Loreta³⁴ first suggested that the star's fluctuations were due to periodically ejected clouds of material. Subsequently O'Keefe³⁵ showed that the material was most likely carbon dust (graphite?) propelled into the ISM by radiation pressure from the star itself. The IR excess which such stars exhibit is consistent with a scattering dusty circumstellar shell which re-emits the absorbed stellar radiation at longer (IR) wavelengths. The dynamics of the ejection process are still to be resolved, in particular, whether it occurs in a spherically symmetric pulsing expansion or according to some less symmetric scenario.

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Apart from copious amounts of dust (grains), we now know that red giants contain large quantities of fascinating carbon molecules and radicals. IRC+10216 has been studied extensively, and to date some 30 or so molecules and radicals have been observed in its envelope. It is pumping vast quantities of gas and dust into the ISM (ca. $10^{-5}M_{\odot} \text{ yr}^{-1}$). Polyynes are intermingled with the dust, and indeed this is the best object for very long carbon chain molecule detection. The first extended carbon-chain radicals CCCN³⁶ and CCCCH³⁷ were detected by Guelin, Green, and Thaddeus, in this fascinating celestial coal mine. Further, equally exciting observations have been made that chains such as C₅H,³⁸ C₆H,^{39,40} C₄CO,⁴¹ and CCCSi⁴² are also produced in this star. Most important are recent findings by Bernath and co-workers, who have detected C₃⁴³ and C₅⁴⁴ by IR spectroscopy. It was the early discoveries of long chains in this star which suggested that such species (polyynes, cumulenes, etc.) must play some key role in the "galactic carbon cycle". Thus their role in stellar dust formation and links with terrestrial soot formation were already an intriguing prospect in the early 1980s.⁴⁵ During cluster beam experiments which probed this possible chain/dust/soot relationship, it was discovered that C₆₀, buckminsterfullerene, could be created spontaneously.¹ The studies also showed that chains with as many as 20 or more carbon atoms also formed^{4,5} and supported the proposal that they might be precursors of larger carbon species,^{18,45} but their specific role was not at all clear. As experiments progressed, it became clear that C₆₀ was produced together with large particles; indeed, it appeared to be a dead-end byproduct perhaps able to throw new light on the carbon dust formation process.² Reactivity experiments by Zhang et al.⁴⁶ were interpreted in terms of a nucleation scheme involving an embryo for the growth of macroscopic carbon particles, and a possible link with soot formation was suggested. Though the latter possibility was criticized,⁴⁷ it appears that little is known about the chemistry of soot formation,⁴⁸ so it is not obvious that any formation process can be discounted at present.⁴⁹ Further analysis and refinement of this nucleation scheme showed that it predicted spiraling spheroidal graphite giant molecules whose onionlike structures matched perfectly⁵⁰ the known concentric polyhedral shell structures of some carbon microparticles observed previously by Iijima.⁵¹ These studies present a very

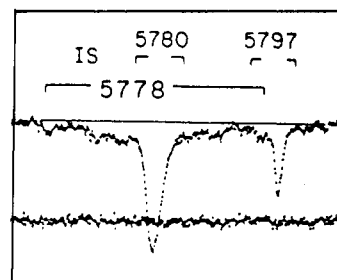


Figure 3. Two relatively strong DIB features which lie on top of a particularly broad feature. Reprinted with permission from ref 57. Copyright 1975 University of Chicago Press, Journals Division.

interesting early insight into the possible structure of interstellar carbon dust (see below).

Astrophysical Problems Involving Carbon Reappraised

There are several problems involving carbon where some links between C₆₀, chains, and dust are possible,^{2,52,53} perhaps even likely, and it is useful to reappraise some of the leading questions in the light of our new understanding. The aim here is to understand these questions better in the hope that answers will soon be forthcoming. Firstly, fullerene-60 analogues are likely to be important in space only if the geodesic cage structure (σ -electron network) remains essentially intact and the integrity of the fullerene π -electron system is disrupted as little as possible. Otherwise a vast range of analogues appears feasible and/or cage fragmentation would be expected to take place. Secondly, as fullerenes are very photostable in cold beams⁵⁴ and exhibit a peculiar instability in some condensed phases,⁵⁵ they may be more stable in space than on earth. The detailed arguments which suggest that fullerene analogues may be the missing links in the galactic carbon chain (of events) have been discussed by Kroto and Jura.⁵⁶

The Diffuse Interstellar Bands (DIBs). The identity of the carrier of the DIBs (a set of some 80 electronic absorption features which are too broad to be atomic lines) has been a major puzzle ever since they were identified as interstellar features in 1936. Two are depicted in Figure 3. Their properties have been summarized by Herbig.^{57,58} Numerous suggestions have been made as to the nature of the carrier, and at present the consensus lies between some moderately large "stable" molecule and grainlike material in which atoms are trapped, giving rise to matrixlike spectra. The problem is that this material appears to be ubiquitously abundant even in the hostile environment of space and yet, astoundingly, has never been identified on Earth. Recently Sarre⁵⁹ and Fossey⁶⁰ have shown convincingly that five DIB features occur in emission from the "Red Rectangle", a carbon-rich star, HD44179, which exhibits

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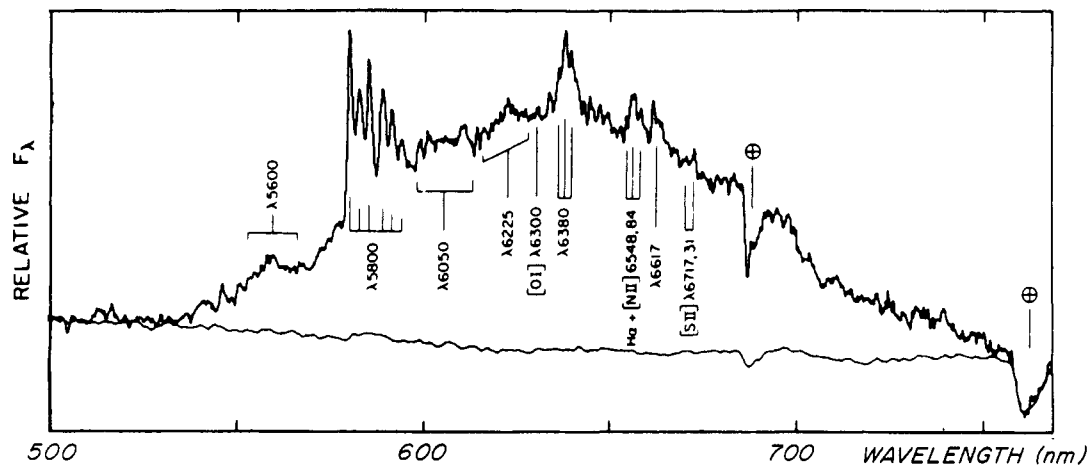


Figure 4. Emission from the Red Rectangle. Reprinted with permission from ref 62. Copyright 1985 Blackwell Scientific Publications Ltd. Certain sharp features in the 5800-Å set have been identified with those in Figure 3 by Sarre⁵⁹ and Fossey.⁶⁰ Note that the sharp features lie on top of a broad continuum.

a bipolar outflow with a roughly rectangular spatial emission pattern. These features are sitting on top of a very broad intense red continuum emission⁶¹ (Figure 4), which Duley has suggested is from some form of H/C containing material.⁶² C₆₀ or an analogue was suggested as a possible carrier when the molecule was first found to form spontaneously.¹ There are intriguing parallels between fullerene-60 and the DIB carrier which have prompted further probing of the conjecture.^{2,52,53,56,63} The ubiquity of <13.6-eV radiation indicates that if C₆₀ is formed in space (and is as stable as beam experiments suggest), it will be ionized. The case for ionic analogues^{52,53} has been discussed.⁶³ The discovery of endohedral fullerene complexes in which the atom is inside the cage⁶⁴ such as (La) has prompted interest in the astrophysical importance of such species, and several calculations have been carried out on their spectra.⁶⁵⁻⁶⁸ Perhaps the most interesting analogues are, however, *exohedral* complexes, and the possibility that charge-transfer bands are associated with such species as (M)⁺ where M is an abundant interstellar species such as Na, K, Ca, Fe, S, O, etc. has been discussed in detail.⁵⁶ These ideas are supported by the recent experimental results of Huang and Freiser.⁶⁹

The Unidentified 2170 Å Band. Another feature which has also been the subject of numerous studies is a strong absorption centered at ca. 2170 Å,⁷⁰⁻⁷² Figure 5. This feature is very strong and in general is always observed at 2170 Å. Stecher and Donn suggested that this was caused by carbon when they first detected the feature.⁷¹ The line shape is also relatively constant although there are one or two objects in which the feature appears to shift slightly.⁷² Interestingly Day and

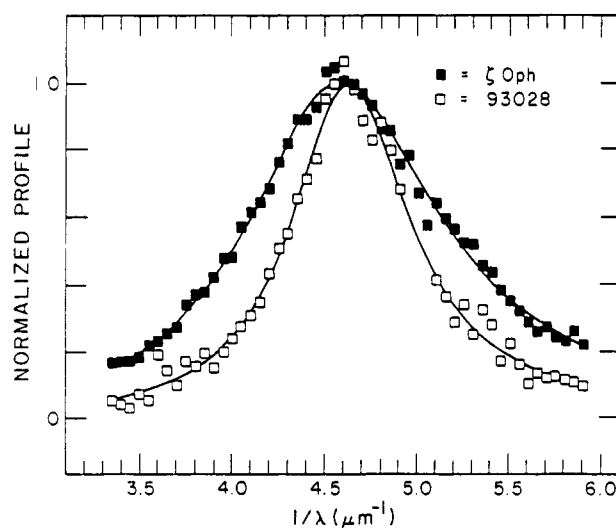


Figure 5. Examples of the broad 217-nm interstellar absorption feature. Reprinted with permission from ref 72. Copyright 1986 University of Chicago Press, Journals Division.

Huffman⁷³ have studied the scattering from pure small carbon particles and find a feature centered near 2400 Å. We note⁵⁶ here that in the highly H-depleted RCorBor stars the feature appears to shift considerably: to ca. 2400 Å.⁷² Protonated species are common in the ISM, and thus it is possible that a protonated exohedral fullerene complex (+)H should be seriously considered.⁵⁶ Such a species is expected to have a very strong, very broad, charge-transfer electronic absorption near 6 eV (ca. 2100 Å),⁵⁶ which is quite close to 2170 Å, so a contribution to the interstellar extinction from such a transition may be important.

The Unidentified Infrared Bands (UIBs). The development of sensitive IR telescopes has led to the detection of IR emission from circumstellar material.⁷⁴ Comparisons between some discrete circumstellar features and laboratory IR measurements of known polycyclic aromatic hydrocarbons (PAHs) are sufficiently good that the assignment to PAH-like carriers is quite convincing.⁷⁵⁻⁷⁷ The C₆₀ discovery suggests that hy-

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drogenated curved/partly-closing structures might also occur, and such objects have been shown to yield certain IR features consistent with observation.⁷⁸

There are of course a multitude of possible species which can form, from some complex mix of small compounds to large aggregates of organic material such as soots and tars. It has been suggested⁷⁶ that the interstellar radiation flux which pumps the observed bands is such that the pattern of emission frequencies detected can be used to set a bound on the size of the emitting species as containing 20–40 atoms. This calculation, however, depends on the assumption that on absorption of a photon the energy is uniformly distributed and the species or grain emits IR radiation with a characteristic thermalized profile. It is not, however, clear that localized chromophore excitation cannot occur due to inefficient energy transfer in heterogeneous aggregates. Intramolecular vibrational relaxation and the relationship with radiative processes are poorly understood even for small molecules and even less so in complex, loosely bound aggregates.

Of course hydrogen is present in copious quantities in most astrophysical objects; however, the observations of Gerhardt et al.⁷⁹ and Howard et al.⁸⁰ have shown that polyynes are a prelude to soot formation and that C₆₀ forms in a sooting flame and can be extracted. There is thus every prospect that fullerenes form wherever polyynes and dust form in space, even in the presence of hydrogen and oxygen. There is still some way to go before the question of how important the role of non-planar carbonaceous networks is during soot formation; however, it should be investigated, as soot formation appears to be so poorly understood.⁴⁸

Interstellar and Circumstellar Dust. The dust in space is a most fascinating material, playing key roles in many important astrophysical processes.⁷⁰ For instance, it appears that grain surface catalysis is the only way to explain the formation of H₂ in space.⁸¹ For the purposes of this discussion we note that the dust in the dark clouds protects molecules from dissociation by starlight and so enables the heat generated on gravitational collapse to be dissipated by low-temperature rotational emission by CO, so allowing later phases of cloud collapse to occur, ultimately to form new stars. Dust certainly forms in the shells of red-giant stars and also around novae, supernovae, and planetary nebulas, and the latter are proving to be rather interesting sources of carbon. The planetary AFGL 2688 is a hot star surrounded by a donut-shaped dense molecular gas and dust cloud.^{82,83} The star sits in the hole in the middle of the donut, and emanating from the star, along the axis of the donut, is a bipolar outflow of high-velocity gas: H and CO at ca. 50 km s⁻¹. The visible emission contour has caused it to be called the "Egg Nebula".⁸² Rieu et al.⁸³ discovered a curious feature

about this star: The donut contained the molecules that the ion-molecule theories^{23,24} readily explain (ammonia etc.), but far out from the center, the conical bipolar outflow is surrounded by a hollow cone of gas, rich in polyynes.⁸³ It has been suggested that these chains are produced by grain fragmentation due to grain-grain collisions.⁸⁴ Carbon cluster beam photofragmentation studies have shown that macroscopic carbon clusters can break down to such chains, and C₆₀ also appears.⁵⁴ Thus laboratory experiments suggest that C₆₀ analogues may also occur in such regions.²

Studies of the polarization of scattered light by interstellar dust suggest that in some regions the dust may consist of elongated particles.⁷⁰ The work of Iijima⁸⁵ and Endo⁸⁶ indicates how such elongated carbon microfibrils may grow under conditions in which C₆₀ forms. Microfibrils with diameters of 30–100 Å with graphite walls containing from 2 to 50 layers of graphite have now been detected. These structures are closely related to the structures observed earlier by Iijima.⁵¹ On the basis of our new understanding of closed carbon giant networks^{2,50} a possible growth mechanism for such microfibrils has been proposed.⁸⁷ The possibility that such tiny tubular graphite structures (zeppelens?) are feasible adds a new dimension to the possible answers to a range of fascinating spectroscopic astronomical observations, such as those by Sellgren, who observed IR emission consistent with microscopic particles of these dimensions.⁸⁸ Wright has suggested that spheroidal graphite structure cannot account for the observed emission.⁸⁹ It should, however, be noted that attention has been drawn to the fact that the apparent epitaxial control of growth in general breaks down and, in later stages of accretion from the gas phase, graphite layers become more chaotic and so-called "amorphous" texture appears to develop.⁹⁰

Meteoritic Carbon. Lewis et al.⁹¹ have detected diamond domains in meteorites. These inclusions are most interesting, and how they might arise is food for thought. One suggestion is that they might form by metamorphism, initiated perhaps by shock waves, of the internal structure of quasi-icosahedral concentric-shell graphite dust included in the meteorite.⁹²

One of the most intriguing aspects of the meteorites is the occurrence of curious isotope anomalies. Clayton⁹³ has suggested that the existence of almost pure ²²Ne in some carbonaceous chondrites might be explained if it is a remnant of ²²Na formed in supernovae. He suggests that the ²²Na (which has a 2.5-yr half-life) is ejected from the star and cocondenses with carbon in the surrounding dust shell. The detection of endohedral metal complexes such as (M) where M = La etc.^{64,69} and the elegant recent observation of He encapsulation during collisions with fullerene-60 by Weiske et al.⁹⁴ suggest that the endohedral fullerene

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complexes might well play a role in these well-known isotope anomalies involving carbon. Soon after the discovery of C_{60} , Heymann⁹⁵ considered the (He) complex from an astrophysical viewpoint.

Conclusions

Several astrophysical problems have been described which involve carbon chains and dust, and attention has been drawn to various chemical scenarios in the laboratory which yield very similar conditions. The cluster beam studies indicate that chains (or their monocyclic ring analogues) form first, which then evolve into fullerenes and carbon microparticles in some yet to be fully understood way. The fascinating observation of Rubin et al.⁹⁶ that C_{30} monocyclic rings dimerize spontaneously to C_{60} can be rationalized by a scheme in which a concerted series of cycloaddition steps can

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result in a graphitic/fullerene network.⁹⁷ Furthermore, recent evidence suggests that fullerenes may even be the direct precursors of pure carbon microparticles accreting carbon directly from the vapor.⁸⁷ On the basis of a wealth of circumstantial evidence, we have argued that fullerene analogues must have an important role in the "galactic carbon cycle". It has been pointed out⁵⁶ that fullerene analogues do have several properties that justify their careful consideration as carriers of some ubiquitous astrophysical features and that, if they are not responsible, there is some other as yet unidentified mystery involving carbon to be unraveled.⁵⁶

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Solid-State Chemistry of Fullerene-Based Materials

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Introduction

The availability of "large" quantities of buckminsterfullerene (C_{60}) and the related fullerenes (C_{70} etc.) has generated an explosion of research activity by synthetic and physical chemists. It is now evident that fullerene-derived solids are equally exciting, from both the fundamental and potential technological viewpoints, and that these solids possess many novel properties of interest to physicists and materials scientists. The 1985

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Kroto/Smalley¹ and 1990 Huffman/Krätschmer² discoveries have indeed provided something for everyone!

In this Account, we summarize what we have learned in the past 12 months about the pristine fullerene solids (or "fullerites") C_{60} and C_{70} and a variety of chemically-modified solids. The emphasis is on synthetic methods, structure determinations, and phase transitions. Finally we describe a new modified fullerene " C_{60} monoxide" which may lead to interesting new solid phases.

Solid C_{60} and C_{70}

The first fullerite solids were grown from benzene solution as crystals with well-developed facets and several different morphologies.² Because these beautiful crystals contained benzene as well as higher fullerenes,³ and were highly faulted, the first X-ray results were misleading and led to an interpretation of a hexagonal-close-packed (hcp) structure for solid C_{60} . Subsequent work showed unambiguously that C_{60} at 300 K adopts the other close-packed structure, face-centered

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