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THE FORMATION AND STRUCTURE OF CIRCUMSTELLAR AND INTERSTELLAR DUST

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ABSTRACT.

The intriguing abundance of long linear carbon chain molecules in some dark clouds and in circumstellar shells is still not well understood. Recent laboratory studies which have probed this problem indicate that when carbon vapour nucleates to form particles, linear chains and hollow cage molecules (fullerenes) also form at more-or-less the same time. The results have consequences for the formation, structures and spectroscopic properties of the molecular and dust components ejected from cool carbon-rich stars. A most interesting result of the experimental observations relates to the probability that a third character in addition to the chains and grains, the C_{60} molecule probably in the form of the ion C_{60}^+ in the less shielded regions, is present and perhaps responsible for some of the ubiquitously observed interstellar spectoscopoic features such as the Diffuse Interstellar Features, the 2170A UV Absorption or perhaps some of the Unidentified Infrared Bands. Further study of small carbon particles which form in the gas phase has resulted in the discovery that they have quasi-icosahedral spiral shell structures. The rolê that such species may play in the interstellar medium as well as that played by C_{60} (or C_{60}^+) should soon be accessible to verification by a combination of laboratory experiment and astronomical spectroscopy.

INTRODUCTION

In 1975 the polyyne H-C≡C-C≡C-C≡N was synthesised and studied by microwave spectroscopy (ref. 1) and the resulting laboratory frequency was then used to detect this species in space by radioastronomy (ref. 2). Subsequently the combined synthetic/microwave/ radioastronomy approach resulted in the discovery of even longer carbon chains in space. The molecules HC_7N (refs 3, 4) and HC_9N (ref. 5) were detected and laid the basis for the detection of even longer chains such as $HC_{11}N$ (ref. 6). More recent work has aimed at an understanding of the formation of chains in space (refs 7-9) and has focused attention on the possibility that they are produced at the same time as dust in carbon-rich red giant stars (refs 10-14).

In order to explore the high temperature stellar route to carbon chain molecules experimentally, a project to study the reactions and spectra of carbon clusters in a beam produced by laser vapourisation was initiated. These experiments successfully confirmed that very long carbon chains (Fig 1) are indeed produced in a plasma when carbon particles form (refs 15, 16). During these experiments a most exciting discovery was made; that a single molecule, C_{60}, was spectacularly resistant to further growth[17]. Indeed it has subsequently been shown that under conditions where almost all the carbon vapour has nucleated

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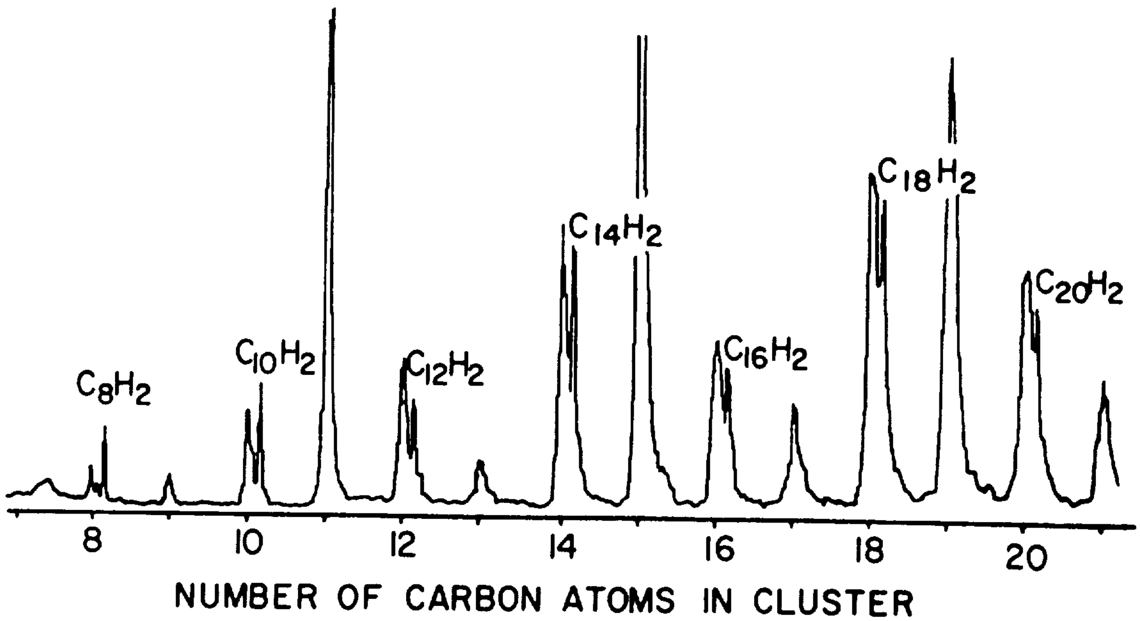


Fig 1 *Mass spectrometric detection of species H-(C≡C)$_n$-H produced by the reaction of H_2O with a beam of carbon clusters. C_n peaks (n even) are accompanied by +2 mass unit satellites.*

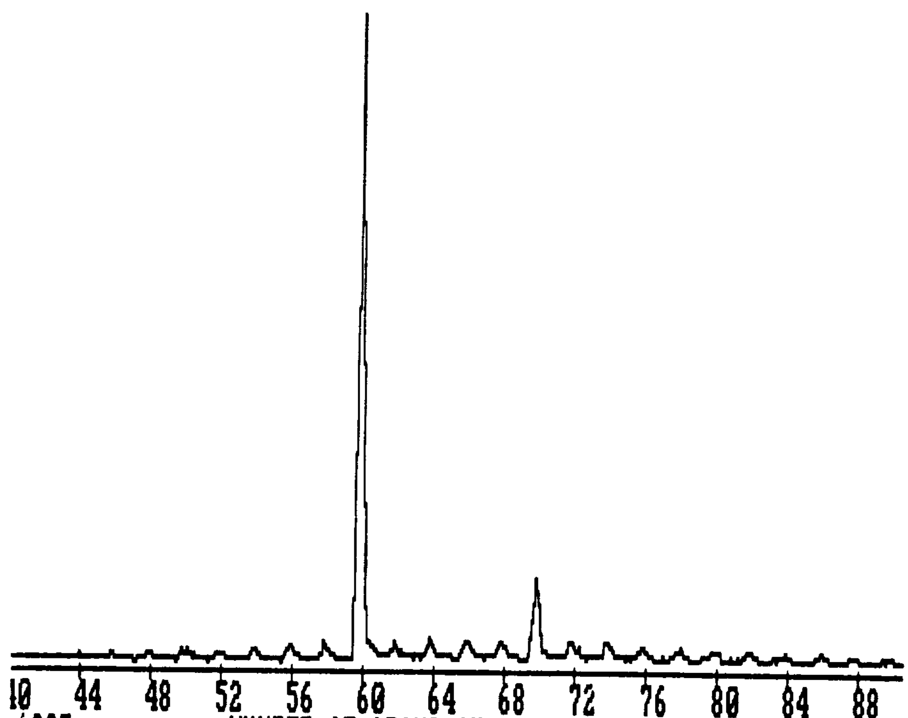
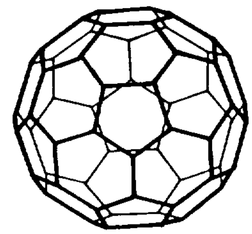


Fig 2 *Mass Spectrum of the carbon clusters which remain* <u>*after*</u> *particle formation has taken place in the gas phase. Note that under these conditions C_{60} and C_{70} are dominant because they are inert to growth.*

to form large particles, C_{60} remains together with some C_{70} as shown in the mass spectrum, Fig. 2. The formation of a specific large molecule in dominant abundance in a chaotic chemical system is a unique observation with many consequences.

The properties of this carbon molecule have been rationalised on the basis of a closed carbon cage with truncated icosahedral symmetry, similar to that of a football, Fig 3. Geodesic and

Fig 3 The proposed truncated icosahedral structure of C_{60} buckminsterfullerene.



aromaticity factors can account readily for the stability of such a molecule. Several further experiments have been carried out relating to the formation of C_n-metal complexes (ref. 18) the reactivity and clustering (ref. 19), negative ion formation (ref. 20) and the relation between the ionic and neutral clusters and their nucleation rates (ref. 21). The results of this programme have recently been reviewed (refs 22, 23). A study of the geodesic and chemical properties of cage structures of various sizes has produced significant support for the buckminsterfullerene C_{60} structure proposal by showing that the magic numbers observed in the carbon nucleation experiments are entirely consistent with the formation of a family of closed fullerene cages (ref. 24). The basic nucleation mechanism (ref. 19) has recently been refined resulting in a detailed new picture of the structure of small carbon particles that nucleate in the gas phase (ref. 25)

The first stages in the hypothetical nucleation mechanism are shown schematically in Fig 4. It is proposed that the mechanism is

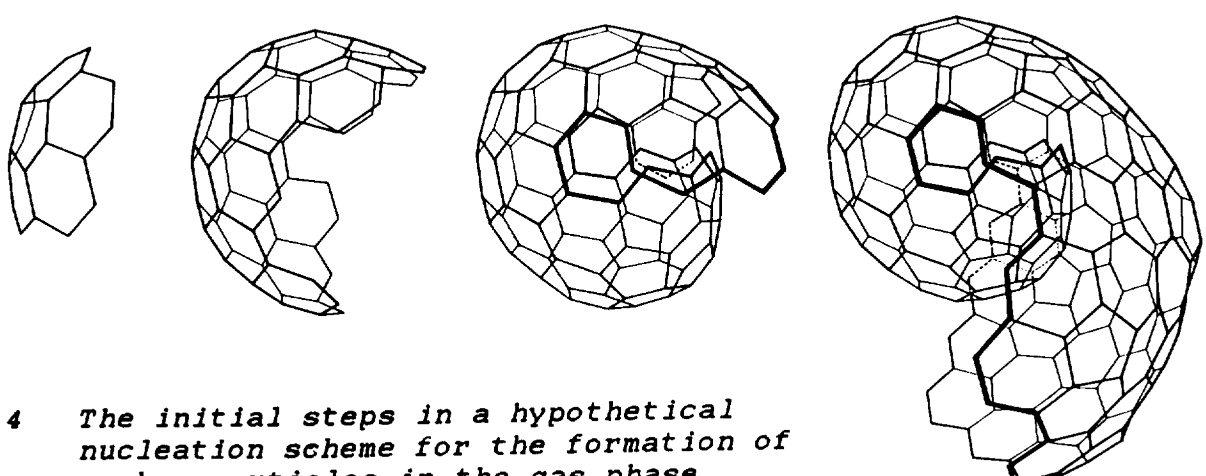
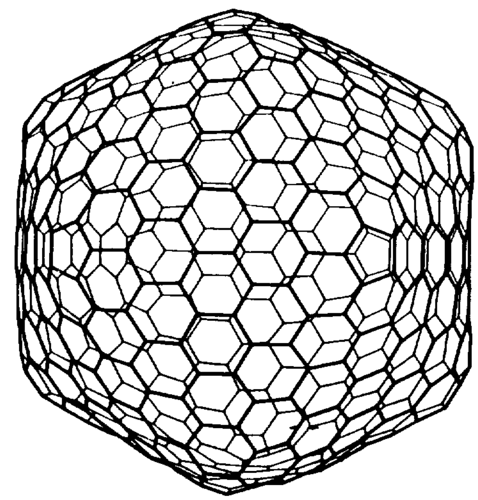


Fig. 4 The initial steps in a hypothetical nucleation scheme for the formation of carbon particles in the gas phase.

governed by two straight-forward principles: 1) Graphitic network formation, in the gas phase, follows a low energy route involving curved, rather than flat, sheets so that edge dangling bonds are eliminated, and 2) epitaxial factors control the subsequent structure of new network. The initial embryos have shell-like shapes, Fig. 4, in which the network involves both 5- and 6-membered rings. The network has bond lengths and angles consistent with those of an extended polyaromatic hydrocarbon in which isolated corannulene segments play key rôles. As the shell grows larger, fresh network forms at an altitude close to 3.4Å (the graphite interlayer separation) above the previous surface. This is achieved most readily by locating the twelve necessary and sufficient pentagons in each turn of the spiral directly over those in the previous segment. This epitaxial growth pattern results in a single particle with structural integrity. As it grows the structure should approximate that of a large closed cage which has been shown to be quasi-icosahedral, Fig 5 (ref. 25). The pentagons in

Fig 5 Large particles consist of concentric spiral shells. The shapes of the larger ones are more-or-less icosahedral, like larger closed cages. The highly symmetric fullerene $(I_h)C_{540}$ is depicted here.



spiral shell particles will be located along twelve radii resulting in a single quasi-crystal consisting effectively of 20 pyramidal micro-crystallite segments. In cross-section such a particle should exhibit a concentric spiral polygonal "ring" pattern. In Fig. 6 is shown one of

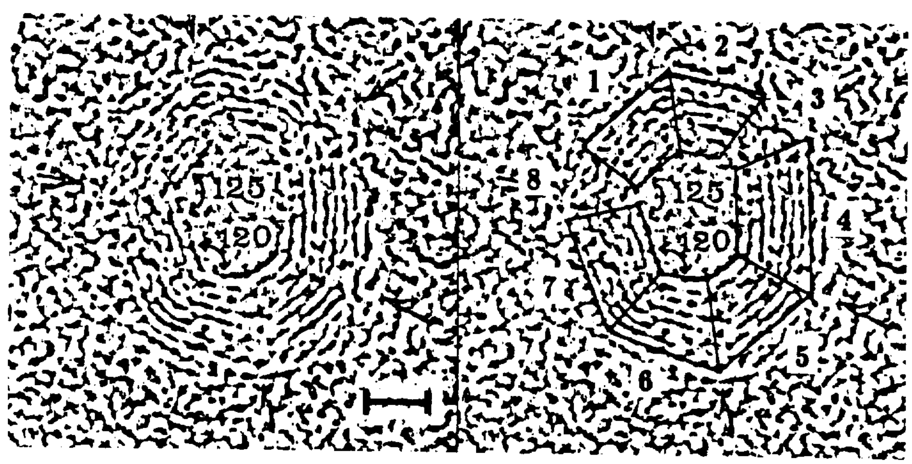


Fig 6 Electron microscope picture of a particle from a carbon arc. The concentric polyhedral shells are clearly evident. The folds in the shells are delineated in RH figure. The similarity in shape with C_{540}, Fig 5, is striking. The marker indicates 20Å and the interlayer spacing is 3.4Å.

the beautiful transmission electron microscope pictures of carbon particles taken by Iijima (ref. 26), is shown. Iijima was able to show clear evidence of such concentric polyhedral shells and the present work has yielded a simple explanation (ref. 25).

In this model, it is clear, that occasionally the pentagons will occur at just the right places for C_{60} to form. When this happens however the reactive edge is lost and further growth cannot occur. Thus C_{60} is predicted to be a by-product of the general carbon nucleation process. Just how much carbon, in general, ends up in this cul-de-sac is an interesting and important question. The mechanism thus accounts for C_{60} and also, for the first time, the detailed structures of macroscopic carbon particles. The mechanism also appears to have the basic ingredients necessary for the solution the old problem of soot (ref. 19, 25). This proposal has recently gained significant support from the discovery by Gerhardt, Löffler and Homann that C_{60}^+ is a dominant ion in a sooting flame (27).

ASTROPHYSICAL IMPLICATIONS OF THE DETECTION OF C_{60}

As far as interstellar problems are concerned it is likely that in the circumstellar shells of carbon stars, processes similar to those in the vapourisation experiments occur and the solid particles known to be ejected from such objects may have similar structures. Such quasi-icosahedral particles may thus be the primary refractory cores which are the nucleation sites for further particle growth in the interstellar medium. Intermingled with these particles will be some C_{60} itself. How prevalent the t-icosahedral C_{60} molecule is likely to be in interstellar space is a most intriguing question, however it must be present whenever carbon particles form as it is a survivor of the clustering process, detected at the same time as chains and carbon particles. Large carbon particles are relatively sensitive to photoionisation laser power as they readily shake down to produce smaller daughter fragments ($n < 100$). On the other hand C_{60} appears to be astonishingly resistant (ref. 18). This behaviour is unique as no other cluster species has shown anything like this level of stability. Indeed most other clusters dissociate at relatively modest photon flux.

From these observations we can draw a number of conclusions that are likely to be significant as far as the structure and properties of carbonaceous interstellar grains are concerned. First of all the results indicate that chains and carbonaceous grains form at the same time and in those regions (such as TMC1 and IRC+10216) where they are both detected the grains are likely to have quasi-icosahedral spiral shell structures. It is possible that the presence of hydrogen will obscure this basic pattern producing perhaps a more spheroidal (less obviously polyhedral) structure. We know that chains and grains are forming in the shells surrounding IRC+10216 and other similar objects from where they are continually being ejected into the interstellar medium. Once in the general interstellar medium they are subjected to the ambient stellar flux and occasional shock waves which are the main agents of molecule destruction. On the basis of these arguments we can draw some interesting conclusions about the astrophysical significance of C_{60} buckminsterfullerene itself.

We know that the resilience of CO is a major reason for its abundance and the fact that it is so much more widespread than other molecules, extending significantly further into unshielded (by grains) regions of space than any other molecule so far detected. It is worth remembering that this widespread abundance only became obvious with the advance in the radioastronomy techniques. The present observations indicate that after ejection C_{60} should be an outstanding survivor in the general interstellar medium, probably as the ion, C_{60}^+, protected by its unique ability to withstand shock-wave and photodissociative processes so drastic that most, if not all, other known molecules are destroyed.

As neither C_{60}, nor C_{60}^+ have dipole moments they cannot be detected by radioastronomy which is the most specific of interstellar analytic techniques. C_{60} has however four ir active fundamental vibrational frequencies though others may become active through resonances and it is likely that the modes will be similar to those of corannulene or coronene which do not involve C-H bonds. During nucleation in the presence of hydrogen, partially hydogenated quasi-icosahedral spiral shell particles should form and such species will also possess vibrational modes of similar frequency, including the C_H modes. Thus such species are likely to give rise to emission similar to that of the Unidentified Infrared Bands for the same reasons that these features have been ascribed to hydrogenated amorphous carbon by Duley and Williams (ref. 28) and to polyaromatic hydrocarbons by Leger and Puget (ref. 29) and Allamandola et al (ref. 30). Soot will give rise to similar emission spectra. The pure carbon species C_{60} and C_{60}^+ should also be extensively distributed and their emission, which will lie at similar frequencies, should be excited by the processes that dissociate all other species.

It is possible to generate complexes of the form $C_{60}X$ in which the atom X appears to reside inside the carbon shell (ref. 18) and during the circumstellar carbon dust formation it is likely that many of the atomic and molecular constituents (other than carbon and hydrogen) which are present may become entangled either molecularly bound in cages or adsorbed/absorbed in and on the spiral structures. Graphite itself forms intercalation compounds with numerous atoms and molecules as do soot and carbon black. Such materials are likely to show electronic spectra which are characteristic of atoms in matrix environments. The resulting lines will lie at determinable frequencies and also may give rise to interstellar features.

From the moment it was discovered it was clear that C_{60} was a most promising possible carrier of various old interstellar chestnuts (ref. 17), such as the Diffuse Interstellar Bands, the 2170Å UV band or the Unidentified Infrared Features. These possibilities should prove amenable to unequivocal laboratory verification in due course. Indeed a very weak absorption band of neutral C_{60} at 3860A has already been detected (ref. 31). Although this wavelength does not coincide with any of the Diffuse Bands this is a difficult region in which to carry out interstellar spectroscopy. This spectrum was obtained by forming a beam containing complexes of the kind $C_{60}\cdot X$ where X was weakly attached by Van der Waals forces. By tuning a dye laser across an absorption band of C_{60} the weakly attached passenger molecule (either C_6H_6 or

CH_2Cl_2) was detached and the event detected by mass spectrometry. This experiment depends on the weakness of the bond between C_{60} and X for two reasons; firstly it is important that the electronic spectrum of C_{60} is not significantly perturbed and secondly that the weak bond can be broken. In the case of the analogous experiments aimed at testing the conjecture that C_{60}^+ is the carrier of some of the Diffuse Interstellar Bands, it has not so far been possible to dissociate the complex (ref. 32). It is possible that in this case charge transfer interactions cause the complex to be too stongly bound for the passenger to be readily detached by this technique and also that the various electronic bands that are expected to occur for the ion are strongly shifted and broadened by the interactions. Numerous bands of the cation are expected to lie in more-or-less the correct part of the visible spectrum as can be estimated by applying Koopmans' Theorem to the various calculations on neutral C_{60} that have been carries out (ref. 33).

Recently there has been a most interesting radio observation by Rieu, Winnberg and Bujarrabal (ref. 34). They have shown that in the Egg Nebula (CRL2688) the central object is surrounded by a small ammonia cloud which lies more-or-less <u>within</u> the dusty envelope which can be seen optically. Most interesting however is their further observation the dusty region is surrounded by second, large, extended molecular cloud in which significant quantities of the cyanopolyyne HC_7N are detected. It is tempting to explain the formation of the chains as starlight photofragmentation products from the outer regions of a large carbonaceous dust cloud and that the presently visible cloud is an inner remnant. It is in just this type of object that our experimental data indicate that C_{60} and C_{60}^+ should remain, as all other material is destroyed.

SUMMARY

These observations can be summarised as follows: Carbon chains and grains are indeed intimately related and it appears that the chains may be intermediates in the formation of carbon particles. They also appear to be produced by photofragmentation of carbon particles as well. The recent laboratory studies suggest very strongly that any dust which is associated with carbon chain molecules should be very similar in constitution to the particles formed in terrestrial carbon nucleation processes, i.e. quasi-icosahedral spiral graphitic shells.

Most interesting conclusions relate to C_{60} itself. In the laboratory we find that whenever chains and carbon particles form so also does C_{60} and, what is more, this molecule is exceptionally resistant to chemical attack and to photofragmentation. Thus in regions such as the outer reaches of the Egg Nebula our experiments point unequivocally to presence of C_{60} and C_{60}^+. The contention that C_{60} may be a ubiquitous character in any carbon nucleation scenario has recently been given further credibility by the observation (ref. 27) that C_{60}^+ is a dominant ion in a sooting flame. It is most satisfying that the proposed carbon nucleation scheme (refs 19,25) predicted that C_{60} should be a by-product of the soot formation process prior to this discovery. The observation lends further support to the contention that the scheme has widespread applicability in that carbon cages can also occur in the presence of hydrogen if the physicochemical conditions are right. C_{60} is unique in that it should also be the LONE MOLECULAR SURVIVOR of the chaotic processes involved in interstellar particle formation and destruction and thus should have a ubiquitous presence in some of the most hostile regions of space. C_{60} and its relatives are most interesting possible carrier for some of the various interstellar spectroscopic features. As the ionisation potential lies between 6.4 and 7.9 eV (ref. 17), in unshielded regions it is most probably ionised as C_{60}^{+} (ref. 14). Thus for the first time an experimentally based scenario can be presented which gives rise to a solitary possible molecule in space. All previous proposals have been unable to account for the single most important fact about the Diffuse bands; the modest number of bands, their relatively constant wavelengths and their correlation properties point to only one relatively large chemically bound carrier, or at most a very small number of such species. On the basis of molecular orbital calculations on the neutral it is clear that it should have only one strong electronic transition in the visible and near uv whereas the ion should possess a modest number, of the order of a few tens.

It certainly seems almost certain that partially hydrogenated analogues of the spiral shell particles considered here will have infra red emission features very similar to polyaromatic hydrocarbons and thus also the Unidentified IR Bands.

It is satisfying to note that some fairly simple concepts now allow many aspects of interstellar and circumstellar carbon chemistry to fall neatly into place.

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