CHAINS AND GRAINS IN INTERSTELLAR SPACE

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ABSTRACT. The intriguing abundance of long linear carbon chain molecules in dark clouds such as TMC1 and in circumstellar shells such as that surrounding IRC+10216 are still not understood. Recent radioastronomy studies are beginning to confirm that more saturated analogues of the carbon chain species are not abundant. Recent laboratory studies indicate that when carbon vapour nucleates to form particles, linear chains <u>and</u> spheroidal shell molecules also form probably as intermediates. The results appear to have consequences as far as the formation, structures and spectroscopic properties of interstellar grains are concerned, in particular those ejected from cool carbon stars.

The polyynes which were discovered in interstellar space as a result of laboratory experiments initiated, originally, for quite a different purpose. They are long molecules consisting of chains of carbon atoms linked by alternating single and triple bonds.

...C≡C-C≡C-C≡C...

Such long linear molecules present some most interesting problems in molecular dynamics and the study of these problems, in the particular case of cyanobutadiyne H-C≡C-C≡C-C≡N (HC_5N) coincided with the break-through in the detection of interstellar molecules by radioastronomy. The observation and analysis of the microwave spectrum of this species (1) seemed particularly significant when connected with the roughly simultaneous realization that the previous member of the family, cyanoethyne H-C≡C-C≡N (HC_3N), was a relatively abundant interstellar species. (2) This abundance and the laboratory radio frequency stimulated a radioastronomy programme to search for HC_5N in space. The molecule was subsequently detected using the NRC 46 m telescope in Algonquin Park in Canada. (3)

At the time the detection of HC_5N was very exciting as it had six (heavy) atoms (C, N or O), two more than any other molecule previously

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detected. A semiquantitative view of the interstellar chemical situation at the time indicated that small molecules with one or two heavy atoms tended to be fairly abundant and that (after two) each successive heavy atom tended to reduce the abundance by a factor of about 10. This rough rule seemed to make sense in the light of some vague statistical reasoning based on the apparent molecular composition of the interstellar medium. Some doubts, however, about the applicability of this rule to the polyyne family began to creep in. Indeed searches for these types of molecule indicated that there were clouds such as TMCI with much higher HC_3N and HC_5N abundances than expected.

The detection of HC_5N, together with its high abundance, clearly promised the possibility of detecting the next polyyne, HC_7N, and urged us accordingly to attempt its synthesis and spectroscopic analysis which resulted in its detection. (4) Not only was HC_7N detected but again the abundance was very high suggesting, now rather persistently, that perhaps there was something special about the chemistry giving rise to these species. The next step, the quest for HC_9N, was obvious, though the route to detection much less so. Takeshi Oka discovered a simple empirical technique which enabled the radio lines of HC_9N to be predicted with quite remarkable accuracy by extrapolating from the known values of HC_nN with n = 1, 3, 5 and 7 which resulted in the detection of HC_9N. (5) The ratios of HC_nN species with n = 3, 5, 7, 9 turned out to be 10:5.0:1.2:0.32, respectively.

It is clear that even longer species can now be sought using the extrapolation technique and indeed a detection of $HC_{11}N$ has been reported. (6)

Ever since the detection of CH, CH^+ and CN in the very early days the problem of how such molecules could form and survive in the ISM has been a major field for study. The detections since 1968 however have injected the study of interstellar chemistry with a new lease of life.

The three main processes which have been postulated are: gas-phase, ion-molecule reactions, grain surface catalysed processes and circumstellar shell formation followed by ejection into the ISM. Of course all three may be important and the balance is certainly not at all clear at present.

Both gas phase ion molecule reactions and grain surface catalysis are, however, presented with severe problems now that substantial concentrations of long chain compounds have been observed. It is certainly not clear that ion-molecule reactions can build up such chains in preference to, say, branched species, especially as branched ions are generally expected to be more stable than non-branched ones. Indeed, if there are analogous branched hydrocarbons and related species in commensurate numbers with the C_n chain molecules, the clouds must contain significantly more molecules than ever considered possible. The questions that must be answered are: Are the polyynes a special case in that interstellar chemistry is geared specifically towards producing them (as opposed to other feasible large species) or are they in fact just the tip of an iceberg? Are there vast hordes of molecules, unknown and as yet undetectable due to lack of sensitivity and other problems? Apart from the possibility of branched carbon chain species there are also numerous linear chain family members which possess various degrees of feasibility.

It is not at all clear that the chains are formed on grains as it is very difficult for them to desorb at the low temperatures that exist in clouds such as TMC1 (c. 10-30 K).

As a consequence of these observations our recent radioastronomy experiments have aimed at determining the relative abundances of molecules related to various polyynes. For instance the molecules CH_2=CHC≡N and HC≡CCH=NH are related to H-C≡C-C≡N by the addition of two H atoms and CH_2=CHC≡C-C≡N is related in a similar way to HC≡C-C≡C-C≡N. Our radio measurements indicate that species with extra H atoms have significantly lower abundances than have the parent polyynes. (7,8) This is a somewhat surprising result in light of the fact that the ratio $C/H = 10^{-4}$.

Our radio data suggest that the answer may lie elsewhere, for instance, one should consider the formation of molecules in the envelopes of cool stars. The cool star, IRC+10216, which has a high carbon to oxygen ratio, has now been shown to be pumping out molecules, in particular the carbon chain compounds. In addition, it seems to be pumping out grains and it may be that in these stars, grains and chains are formed at roughly the same time.

Suffice it to say that interstellar studies have shown that some very long molecules exist in space. They may be very long indeed and their relationship with grains is far from understood and in fact, it is only now that a possible relationship can even be contemplated. The long chains may be an intermediate form of carbon between the well-known small species consisting of one, two or three carbon atoms and particles with high carbon content such as soot. Douglas has suggested that the chains may be responsible for the Diffuse Interstellar Lines. (9)

The main conclusion reached after several years of trying to explain the origins of the long carbon chains we had detected in the ISM was that some new laboratory experiments were called for. In particular studies of efficient chain synthesis routes and the mechanisms of carbon particle nucleation were necessary. New spectroscopic studies of carbonaceous material might also yield clues about interstellar spectra in the infra red and visible - particularly with regard to the carrier of the Diffuse Interstellar Lines.

If gas-phase or surface-catalysed reactions are responsible for the polyynes it should be possible to prove this in the laboratory. On the other hand the detection of carbon chains in circumstellar shells suggests that carbonaceous particles are intimately associated with the processes which produce the chains. Perhaps the chains can provide a key to unlocking some of the numerous problems associated with interstellar grains themselves.

At Easter 1984 I visited Rice University (in Houston, Texas) and saw the elegant work being carried out by Rick Smalley's group. Smalley and his colleagues have developed a powerful technique for producing and studying cold metal clusters by using a focused pulse of intense laser light to vaporise material from a solid surface. (10) The clusters are entrained in a pulse of helium gas and then expanded through a supersonic nozzle, skimmed to produce a beam and interrogated by a second laser which produces cluster ions whose constituents can be determined by mass spectrometry. The apparatus seemed ideally suited to the study of carbon aggregates and so I returned to Rice last September (1985) to follow up this approach in a collaborative study of the interstellar problem with Bob Curl and Rick Smalley together with graduate students, Jim Heath and Sean O'Brien.

Almost immediately we were able to show that the same polyynes that we had detected in space are readily produced in the vapourisation process and that much longer linear chains with as many as 20 or more C atoms were also produced. (11)

During the experiments a bizarre and, at the time, quite bewildering effect was observed in that the signal for one particular cluster, that for C_{60}, (which had always been prominent) became, unaccountably, overwhelmingly stronger than the rest. So much so that under certain conditions it was some 30-40 times stronger than the nearest neighbours, accounting for over 50% of the <u>observed</u> cluster population between C_{40} and C_{100}. At first sight it appeared that the C_{40}-C_{100} species consisted of sheets of hexagons blown away from the graphite surface as essentially <u>intact</u> hexagonally disposed arrays of C atoms somewhat like fragments of <u>flat</u> chicken wire mesh. The prominence of the C_{60} peak was difficult to rationalise on this basis as we could find no obvious reason why a 60 atom sheet should show so much more stability than any other.

After much conjecture we came to the conclusion that stability and unreactivity might be achievable if the sheet had somehow rolled into a closed spheroidal shell and so eliminated its reactive edges. Such a structure would be much like the geodesic domes of Buckminster Fuller and in fact his ideas guided much of our reasoning and played an important part in the quest for a solution to the structure of C_{60}. We came to the conclusion that the structure of the C_{60} molecule is a truncated icosahedron. (12) This beautiful shape has 60 vertices, 12 pentagonal and 20 hexagonal faces and satisfies the tetravalency condition of carbon in a truly elegant manner.

There is a parallel here with Kekulé, who proposed that the properties of the compound benzene, (C_6H_6), could be rationalised if the C atoms were arranged in a ring, in that here we propose the next step - to the surface of a sphere.

We subsequently discovered that Daedalus (David Jones) in the New Scientist (13) in a remarkably imaginative article proposed that hollow molecules might be made if a graphite sheet could be curled up by introducing into a graphite array of hexagons some pentagon inducing impurity atoms. We also discovered that Bochvar and Gal'pern had discussed the properties of a hypothetical molecule with exactly this structure in 1973. (14)

Perhaps the most remarkable aspect of the C_{60} work lies in the discovery that such an object forms spontaneously. We believe such structures actually form naturally (though imperfectly) but they tend to have smaller spheroidal structures inside in onion-like configurations. We propose that such structures explain why soot particles are made up of concentric spheroidal shells of hexagonal graphitic sheets consisting mainly of C atoms.

The results have a direct astrophysical aspect in that they also imply that such structures are likely to be ejected (together with chains) from stars into interstellar space. Although the C_{60} molecule itself may not be the major species it now seems likely that the circumstellar grains are indeed formed at the same time as the chains and their formation and morphology are likely to be governed by the phenomenon that we have discovered - that carbon spontaneously clusters in the gas phase into spheroidal structures. The inertness of soot and carbonaceous particles in general is also explained as the results suggest that the reason for the spheroidal structure is a spontaneous drive towards the elimination of the reactive edges of the carbon sheet as it forms in the gas phase.

As far as interstellar problems are concerned it is likely that in the circumstellar shells of carbon stars, processes not dissimilar to those in these experiments occur and the solid particles which are known to be ejected from such objects are likely to have spheroidal structures as a consequence of the same mechanism that forms C_{60} itself. How prevalent the t-icosahedral C_{60} molecule is likely to be in interstellar space still remains to be determined. It appears to be a survivor of the rapid clustering process which produces spheroidal structures of random sizes. Some structures are fortunate in that as the shell builds up, from small carbon species, they have the correct configuration to close exactly. The majority however do not, leaving a reactive overlapping edge which can progress on to form further outer shells in a complex 2-dimensional spiral. (15)

We have seen from our measurements that the larger 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. (16) 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 suggest that chains and carbonaceous grains will generally tend to 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 spheroidal graphitic structures. We know that chains and grains are forming in the shell 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.

After ejection the outstanding photostability that C_{60} displays should enable it to withstand all but the most severe radiative (and, we believe, shock-wave) conditions. We know that the resilience of CO is the main 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. The present observations indicate that C_{60} might survive in the general interstellar medium (probably as the ion C_{60}^{+}) protected by its unique ability to survive processes so drastic that, most if not all, other known molecules are destroyed.

As C_{60} has no dipole moment it cannot be detected by radioastronomy which is the most specific of interstellar analytic techniques. It has however four ir active characteristic fundamental vibrational frequencies. It is likely that these will be somewhat similar to those frequencies of corannulene and coronene which do not involve C-H bonds and some of the frequencies of the unidentified Infra Red emission features. The general spheroidal carbonaceous structures, which we propose as possible forms for carbonaceous particles such as soot and interstellar grains (15) are also likely to possess similar characteristic frequencies and as they will contain significant numbers of H atoms in general they will also possess the C-H vibrational modes. It has been shown by Duley and Williams (17) that the correspondence between the UIR features and polycyclic aromatic hydrocarbon (PAH) frequencies is good and Leger and Puget (18) have shown that coronene also shows a good fit. Although it is not clear just how the emission spectrum will correspond with the absorption spectrum, it is likely that the fundamental frequencies detected in absorption will be important. These studies present relatively convincing evidence that the UIR features are associated with molecular material in which carbon rings are present. It is likely that the IR emission of soot will give rise to somewhat similar features. C_{60}

should be even more extensively distributed and its emission excited by pumping processes so violent that other species are dissociated.

We have also seen that under certain circumstances it is possible to generate complexes of the form $C_{60}X$ in which we believe the atom X resides inside the carbon shell. (19) During the carbon grain formation process it is likely that many of the atomic and molecular constituents (other than carbon and hydrogen) which are present in the ISM are almost certain to become entangled in the resulting three dimensional structures either molecularly bound or adsorbed/absorbed. It is well known that graphite itself forms intercalation compounds with numerous atoms and molecules, and that soot and carbon black particles do so in a similar fashion. Such species are likely to show electronic spectra which are characteristic of atoms in ligated situations and thus broadened by the pseudo molecular environment. The resulting lines would lie at precisely determinable characteristic frequencies and so if these types of complexes or C_{60} and its bare colleagues are responsible for any interstellar features such as, for instance, the Diffuse Interstellar Bands, the 2170Å uv band or the Unassigned Infra Red emission features, the assignment should prove amenable to verification in due course.

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DISCUSSION

A. Léger : 1) In connection with astrophysical conditions, have you tried to introduce H_2 in the system ?

2) If you start building planar structures (hexagons) how can you bend the structure and close it even if it is energetically more stable ? The kinetics seem to be difficult to explain.

Answer : 1) A careful study of the formation of large cluster population in the presence of hydrogen (H_2 or H) has not been carried out as yet. This is a very important experiment especially for C nucleation in circumstellar (or any other interstellar) environment.

2) Whatever the difficulty in explanation, the data are inequivocal: C_{60} is a very special object and our explanation is not only elegant but has yet to be shot down.

d'Hendecourt : How specific is this experiment ? Can the conditions of the experiment applied to astrophysical cases (grain nucleation in circumstellar shells) ?

Answer : We have obtained widely different results as the clustering conditions are varied. In particular, they are slightly dependent on the He pressure and the timing of the vaporization laser pulse relative to the arrival of the He pulse over the target graphite surface. The situation appears to be very complicated but three observations can be made. If the vaporization laser is fired before the He pulse only small clusters are detected; during the pulse both small and large (C_{60} prominent); after the pulse only large clusters are seen. And all variations between.

We have deliberated long over these observations, and have not yet reached a good rationalization. I suspect that at low pressure wall effects are important.

S. Mukamel : What is the relative stability (energy) of the football component with other structures ? Does it compensate for the loss of entropy ?

Answer : I am not sure that entropy is as important at second sight as it appears at first sight. We must ask what is the relative entropy difference between a 'perfect' hexagonal sheet and a closed shell with pentagonal 'defects' ? There is a paper in press (JACS) on this stability which confirms our conjecture that the closed Buckminsterfullerence for C_{40} - C_{100} are more stable than graphitic sheets of similar size.

H.C. Siegmann : The stability of the C_{60}La-cluster: Can it be explained by assuming that La is located in the center of the soccer-ball ?

Answer : The data indicate that C_{60}La or C_nLa (n, even) are more stable than the bare Cn clusters (C_{60} αC_{70} perhaps excepted). If the clusters we see were 'say' flat plates with La attached one might expect $C_{60}La_n$ with n > 1 etc. to be as detectable as C_{60}La. The data suggest **one** and only one very special site and the centre of a sphere fits such an observation well if not better than anything else we have thought of.

Lou Allamandola : 1) For this very symmetric molecule, there must be only a few IR allowed transitions. Have you done the group theoretical analysis to determine how many of the 180 vibrations are IR active - and if so - do you have any idea where they are ?

2) Could the observation that when you vaporize the graphite after the He pulse has passed shows primarily this smaller chain-like clusters while vaporization before produces the larger clusters be a consequence of the inherent stabilities of these two forms ? Stein has some theoretical results which indicate that when C atoms are to produce clusters/molecules above ~ 3000° C linear chains are favored, while below, PAHs are.

Answer : 1) Again this problem has been addressed by Bell Labs theoreticians (in press) who find that only 4 vibrations are allowed by symmetry. I think that soon there will be reliable estimates of these frequencies. They should be fairly susceptible to standard free field calculation.

2) The conditions are actually the reverse. I hesitate to present an explanation for these observations even though my colleagues and I have deliberated for many hours over them.

d'Hendecourt : After the experiment, were you able to 'save' these clusters in order to study them with various methods (X-ray crystallography, visible/IR spectroscopy) ?

Answer : We are of course trying to collect viable quantities of the products of vaporization, C_{60} in particular, but at present there are non-negligible technical problems associated with this which we hope soon to overcome.

T.J. Wdowiak : What is the repetition rate and can you use gases such as Argon instead of helium so the species can be matrix isolated for optical spectroscopy ?

Answer : Rate: 10 Hz. Up to 50 % Ar has been mixed with the He and without upsetting the conditions under which C_{60} predominates. Above 50 % and up to 100 % the production of C_{60} is diminished. I suspect that this experiment also should be redone in more detail.

Tramer : Have you any data or predictions about C_{60} electronic spectra ?

Answer : A group at Bells Labs have a paper in press on the optical spectrum which indicates that in the UV-visible only one transition is allowed and it is expected to have a very large oscillator strength.

Greenberg : Have you looked into the ultraviolet absorption properties of C_{60} ? Its form seems to suggest a spherised conducting shell of fixed size so that it would make a nice candidate for the 2200 Å band.

Answer : We are attempting to observe the RZPI spectrum using the whole range of accessible laser dyes. I suspect that carbonaceous interstellar matter could be spheroidal shells and the UV absorption should be considered as a candidate. This is just one of the many experiments which we are hoping to carry out on C_{60} and its relatives.