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Effect of trace elements on carbon microparticle formation

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Abstract. Laser vapourisation cluster beam experiments have been carried out to probe the way in which the presence of elements such as O, H, Fe etc. affect the mechanism of carbon microparticle formation. Studies with oxygen and hydrogen are designed to probe the intermediates involved in combustion processes and preliminary experiments with iron are aimed at a study of the characteristic clustering behaviour that occurs in steels. In this work a new carbon oxide $C_{60}O$, oxobuckminsterfullerene, has been identified.

Keywords. Trace elements; microparticle formation; laser vapourisation; clustering behaviour.

1. Introduction

In recent years cluster research has developed into a very important field with applications in many branches of science (Andres *et al* 1989). Perhaps one of the most important aims of cluster science is the determination of the structures of small cluster aggregates and relating these to bulk phase structures. Such structures differ significantly from those in bulk phase and a major goal is the development of materials with novel properties using cluster techniques.

This difference in cluster and bulk phase structure is shown by the element carbon. Bulk carbon is known to exist in two main forms: diamond and graphite having 3-D tetrahedral and 2-D layered structures respectively. However, carbon clusters which can be produced by laser vapourisation of graphite in a high pressure supersonic molecular beam are found to have completely different structures from bulk carbon. In particular, large carbon clusters, $C_n(n = 20 - 600)$ appear to have closed cage structures (fullerenes). This type of structure is typified by the remarkably stable C_{60} species which is believed to be a spheroidal shell with a truncated icosahedral 'Buckminsterfullerene' structure which resembles a football (figure 1) (Kroto *et al* 1985). The properties of these clusters (e.g. high stability, inertness) are expected to be quite different from the bulk phase and may offer interesting technical applications in the future.

This novel molecule contains a central cavity ≈ 7 Å in diameter which is found to be a strong binding site for several types of atoms (Kroto *et al* 1985). This paper

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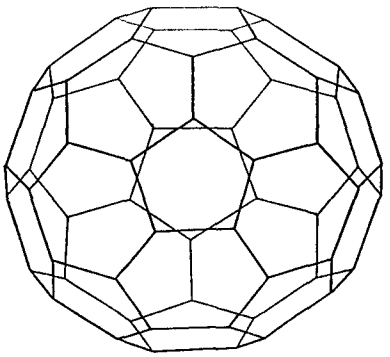

Figure 1. Buckminsterfullerene, C_{60}.

presents the preliminary results of reactions which occur when carbon nucleates in the presence of elements such as oxygen and iron.

A new carbon–oxygen compound $C_{60}O$ where we believe the O atom is trapped inside the cage has been detected. This species is particularly interesting in that this species may also occur during combustion. Similar conditions may also occur when carbonaceous dust forms in astrophysical objects such as stars, and objects such as supernovae in which some meteorites may originate, and so this oxofullerene should occur in space and may be responsible for interstellar spectral features.

2. Experimental

Carbon clusters are created by the laser vapourisation of carbon from the surface of a solid rotating disk of graphite (3 cm diameter) into a high density helium flow (5–100 psi backing pressure). The vapourisation radiation (second harmonic of a Nd:YAG laser at 532 nm) is focused with a lens ($f = 100$ cm) through a 1 mm diameter hole in the cluster source giving approximately 5 mJ energy per pulse (4 Hz) at the target disk. The pulsed nozzle which governs the helium flow is of a double-solenoid design and produces pulses of 200–600 μs duration (Tuennies and Winkelmann 1977; Lubman and Jordan 1985). The resulting carbon clusters are supersonically expanded and then skimmed into a 10 mm diameter molecular beam. The cluster packet is photoionised by an ArF Excimer laser pulse (193 nm, 6·42 eV energy) and the resulting ions are detected by TOF-MS using an 18 mm diameter dual multichannel plate detector. Figure 2 shows the side view of the experimental set-up and figure 3 shows the schematic diagram of the control unit.

$C_{60}O$ is produced when approximately 20% of oxygen is mixed in with the helium carrier gas, whereas, for $C_{60}Fe$, iron pentacarbonyl, $Fe(CO)_5$ vapour was introduced into the helium carrier gas.

3. Results and discussion

Figure 4 shows a spectrum of high mass carbon clusters obtained using very low ionisation power (20 mJ). Notice that the C_{60} peak is very much stronger (≈ 10 times

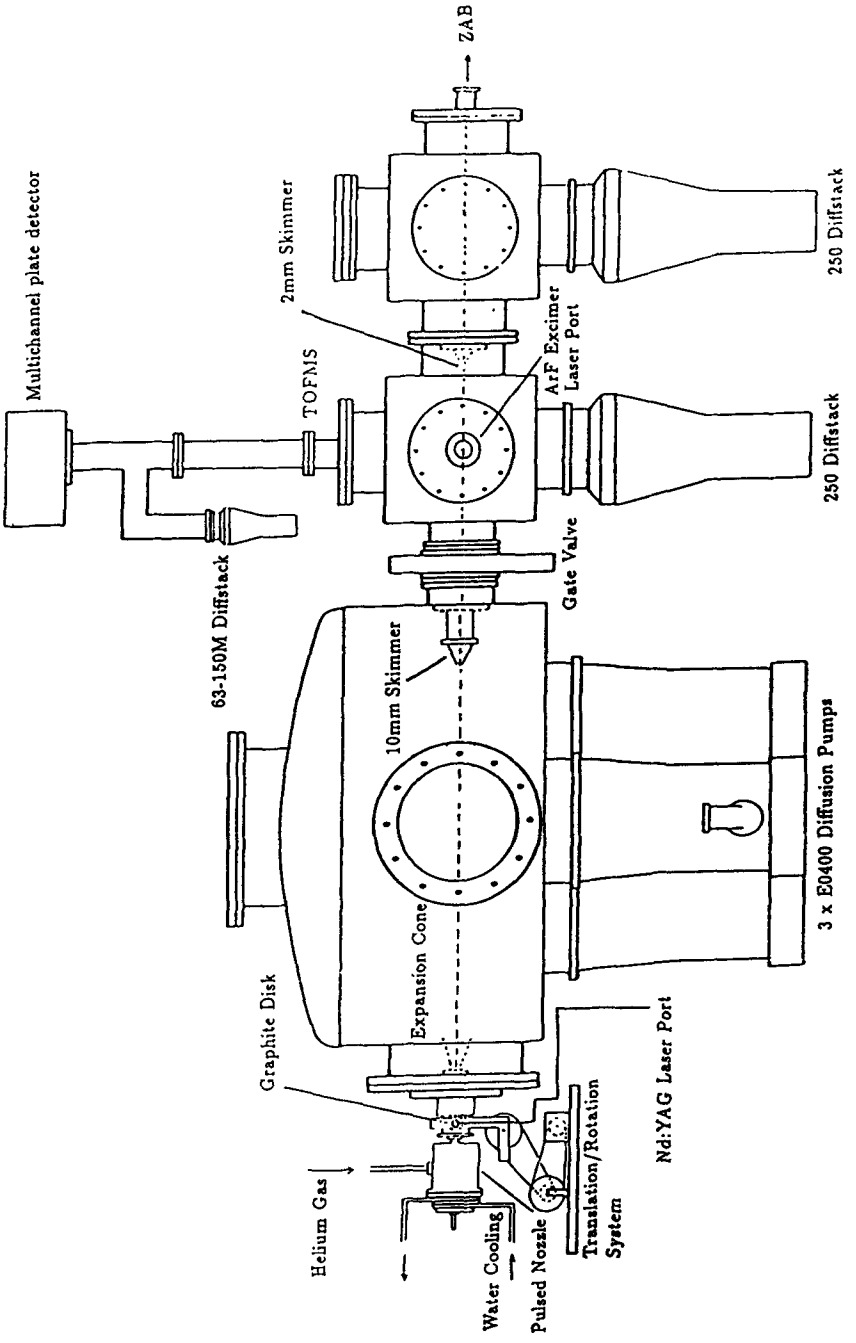

Figure 2. *A side view of the experimental set-up.*

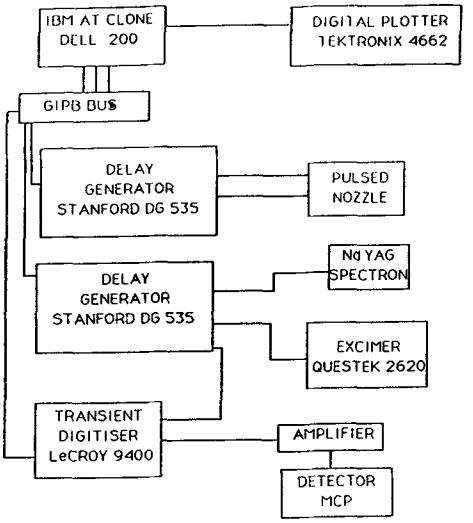

Figure 3. Schematic diagram of the control unit.

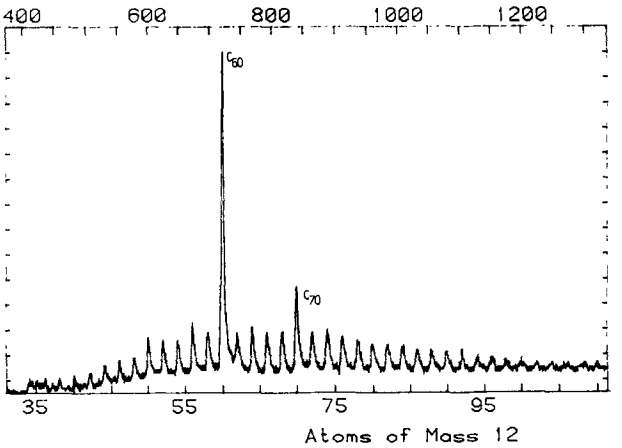

Figure 4. TOF-MS of high mass carbon clusters obtained using very low ionisation laser power (1 attenuator, no lens, 500 shots and razor blades [1 mm]).

that of C_{62}) than those surrounding it. This effect is due to the inertness of this species to further nucleation and is consistent with its highly stable, closed cage structure. However, other clusters which are not so stable are reactive and rapidly nucleate to form large particles beyond the range of the spectrometer.

Figure 5 on the other hand was obtained at much higher ionising laser power where we see that the occurrence of C_{60} is diminished and is no longer quite as dominant. Here large carbon particles are being photofragmented down to smaller clusters which now appear in the spectrum. It is important that experiments are carried out at low ionising fluences so that non-fragmented cluster distribution which is characteristic of the original cluster distribution at the source is obtained.

Figure 6 shows a mass spectrum of large carbon clusters when approximately 20% of oxygen is mixed in with the helium carrier gas. Note that a new peak appears at

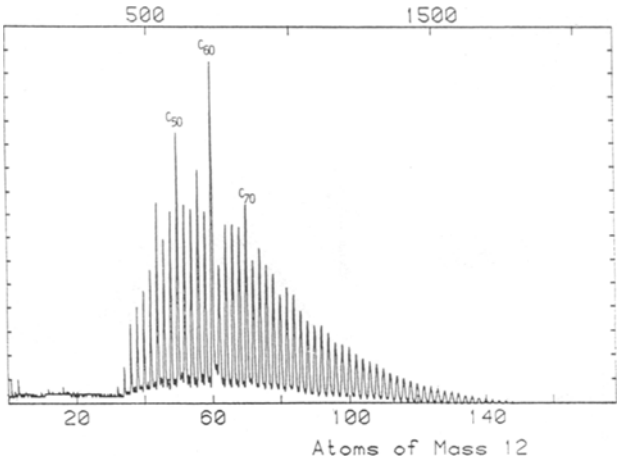

Figure 5. TOFMS of carbon clusters obtained using high ionisation laser power (5 attenuators, lens and 1000 shots).

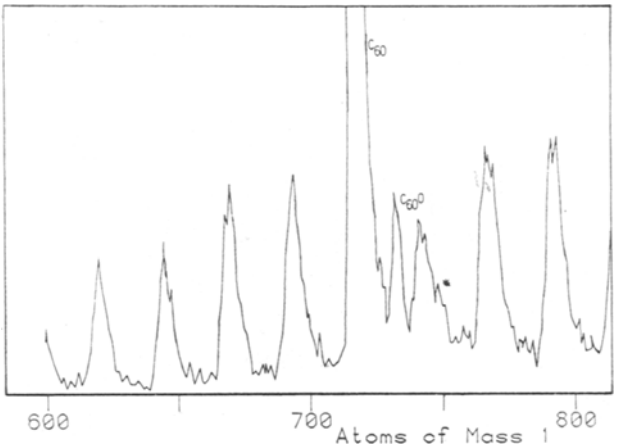

Figure 6. TOF-MS of large carbon clusters when approximately 20% of oxygen is mixed in with helium carrier gas. The asterisk indicates a shoulder that may correspond to $C_{60}O_2$.

720 + 16 amu indicating the formation of a $C_{60}O$ complex. There is also a little evidence for a $C_{60}O_2$ complex. Since the diameter of the C_{60} molecule is about 7 Å there should be enough room to trap O or even O_2 inside the fullerene cage during the primary nucleation step (figure 7). The complex probably forms as the hot carbon plasma expands into the He/O_2 carrier gas pulse producing O atoms which can participate in nucleation.

Figure 8 shows the spectrum obtained when iron pentacarbonyl [$Fe(CO)_5$] vapour was introduced into the helium carrier gas. This experiment was initially aimed at producing the $C_{60}Fe$ complex but as can be seen from the spectrum a weak peak at the position of $C_{60}O$ was seen instead. This suggests that carbon monoxide has been decomposed in the plasma to form the oxygen complex. Experiments with CO gas are now being undertaken to investigate this behaviour in more detail. A further attempt at obtaining the iron complex was undertaken by coating the surface of the

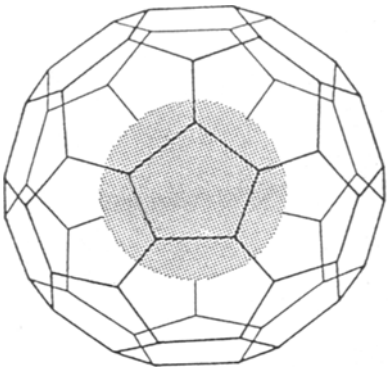

Figure 7. Schematic diagram of a metallofullerene complex, $C_{60}M$.

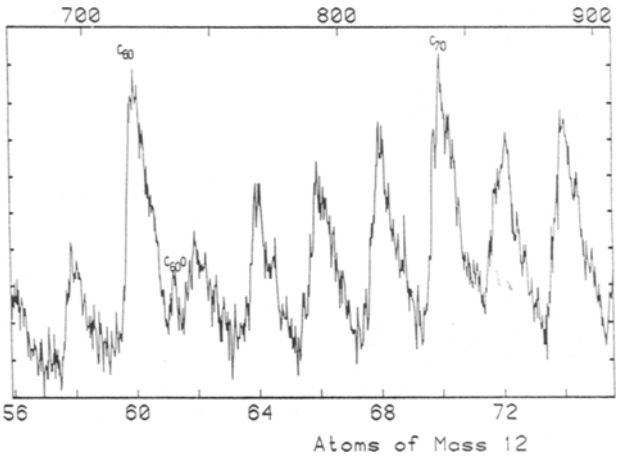

Figure 8. TOF-MS of large carbon clusters when $Fe(CO)_5$ vapour is introduced into the helium carrier gas.

carbon target disc with ferrocene [Fe(cyclopentadienyl)$_2$]. No evidence for FeC_n complexes was detected.

These initial investigations suggest that perhaps carbon prefers to be surrounded by iron rather than the other way around. This may have important implications in the structure of carbon in steels as well as carbonaceous inclusions in meteorites.

4. Conclusions

The discovery of $C_{60}O$ complexes has important ramifications in several areas, in particular astrophysics, considering that oxygen is the third and carbon the fourth most abundant element in the Universe. Thus in regions where carbon is nucleating often in the presence of significant amount of oxygen, it is highly likely that $C_{60}O$ will also form. How important this type of molecule might be is still open to question. However there is also now the distinct possibility that a significant amount of $C_{60}O$ might form and if so may be a contributor to various interstellar spectroscopic features.

The results further strengthen the case for the closed cage football structure of C_{60} with a central binding site. The preliminary results with iron are also interesting in that they suggest that not all metals are able to form stable complexes with C_{60}. Our previous work suggests that alkali and alkaline earth metals have the great propensity for forming metallofullerence complexes. Detailed study of the physico/chemical factors which governs the formation of stable complexes is one of the main aims of the present programme.

References

Andres R P, Averback R S, Brown W L, Brus L E, Goddard W A III, Kaldor A, Louie S G, Moscovits M, Peercy P S, Riley S J, Siegel R W, Spaepen F and Wang Y 1989 *J. Mater. Res.* **4** 704

Kroto H W, Heath J R, O'Brien S C, Curl R F and Smalley R E 1985 *Nature (London)* **318** 163

Kroto H W, Heath J R, O'Brien S C, Curl R F, Zhang Q, Liu Y, Tittle F K and Smalley R E 1985 *J. Am. Chem. Soc.* **107** 779

Lubman D M and Jordan R M 1985 *Rev. Sci. Instrum.* **57** 1884

Tuennies J P and Winkelmann K 1977 *J. Chem. Phys.* **66** 3965