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Production and Discovery of Fullerites: New Forms of Crystalline Carbon [and Discussion]

Wolfgang Kratschmer, Donald R. Huffman, M. Jura and S. Leach

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Production and discovery of fullerites: new forms of crystalline carbon

By Wolfgang Krätschmer[1] and Donald R. Huffman[2]

[1] *Max Planck Institut für Kernphysik, 6900 Heidelberg, P.O. Box 103980, Germany*
[2] *Department of Physics, University of Arizona, Tucson, Arizona 85721, U.S.A.*

Small carbon grains are assumed to be the carrier of the prominent interstellar ultra violet absorption at 217 nm. To investigate this hypothesis, we produced small carbon particles by evaporating graphite in an inert quenching gas atmosphere, collected the grains on substrates, and measured their optical spectra. In the course of this work – which in the decisive final phase was carried out with the help of K. Fostiropoulos and L. D. Lamb – we showed that the smoke samples contained substantial quantities of C_{60}. The fullerene C_{60} (with small admixtures of C_{70}) was successfully separated from the sooty particles and, for the first time, characterized as a solid. We suggested the name 'fullerite' for this new form of crystalline carbon.

1. Introduction

The production of laboratory analogues of interstellar grains was the initial aim of our research. In the autumn of 1982 while one of us (D.R.H.) was a Humboldt Fellow at the Max Planck Institute of Nuclear Physics in Heidelberg we decided to study the optical spectra of carbon grains. We felt challenged by the intense, strong interstellar ultra violet (UV) absorption at 217 nm which it had been proposed was due to graphitic grains (see, for example, Stecher 1969). The arguments in favour of such carriers are based primarily on calculations of the absorption of small, almost spherical, particles which exhibit the dielectric functions of graphite (for more recent literature see, for example, Draine 1988). There had already been very early experimental attempts to produce graphitic smoke particles by almost the same technique that we later applied to C_{60} production (see, for example, Day & Huffman 1973). The results provided some support for the graphite particle hypothesis, however, there were serious mismatches, especially with the width of the interstellar band (see Huffman 1977).

2. Carbon smoke particle production

First we repeated the older smoke production experiments, in which graphite rods were evaporated in a quenching atmosphere of helium. A conventional bell-jar carbon evaporator was used for this purpose. The carbon was vaporized by resistive heating, i.e. by passing a current through a pair of touching graphite rods. Helium pressures ranging between a few to *ca.* 20 torr were used to cool and to promote nucleation and aggregation of atoms and molecules in the carbon vapour into small solid particles. The smoke was collected at different positions within the bell jar,

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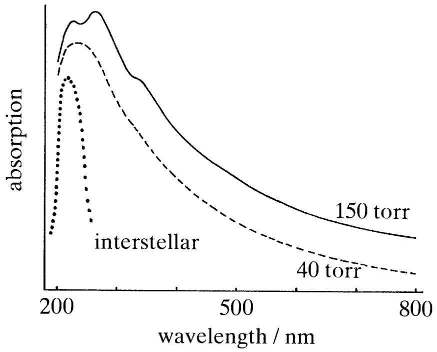

Figure 1. Absorption spectra of collected carbon particles produced by evaporating graphite in a quenching atmosphere of helium. The samples were obtained at different quenching gas pressures. Notice the occurrence of additional absorptions in the UV-visible at elevated helium pressures. These features turned out to originate from C_{60} (buckminsterfullerene). For comparison, the interstellar 217 nm absorption is also shown.

measured spectroscopically in the UV-visible range and examined by means of a transmission electron microscope. When the helium quenching gas pressure was chosen appropriately (*ca.* 20 torr), the spectra of the soot samples peaked at *ca.* 220 nm, i.e. at about the position of the interstellar feature. In all the spectra, however, the widths of the measured extinction curves were much greater than those calculated for graphite particles and also the observed interstellar feature (see figure 1). Part of this discrepancy may be due to the unavoidable clumping of the laboratory-produced particles, which to this day is a major experimental problem. Clumping increases the effective grain size and changes both the effective shape and optical properties of the particles. Another reason for the mismatch may lie in the carbon structure of the grains. Judging from Raman data, the particles we produced consisted of rather disordered graphite (see Huffman & Krätschmer 1990). Grains that have a more ordered graphitic structure are expected to show absorption features with considerably smaller widths.

It may appear that our smoke experiments did not yield much in the way of new insights, however, an interesting effect occurred which caught our attention. At our standard 20 torr helium quenching gas pressure we occasionally observed three additional features superposed to the continuum besides the 'regular' soot absorption feature (see figure 1). This three feature pattern appeared sometimes strong, sometimes weak, sometimes it was absent. Having no explanation, we whimsically called these additional features the 'camel humps'. Only a few observations were made on the carrier of the humps: the samples showed a peculiar Raman spectrum (Huffman & Krätschmer 1990), and the humps disappeared when the sample was heated in air. After much discussion we concluded that the carrier must be an artefact or 'junk'. This did not appear unlikely since the soot, with its high specific surface area, should be able to sweep up various contaminants, such as the pump oil or the vacuum grease which we used in the bell-jar evaporator. We then tried to produce unclumped grains, and in the following years turned our attention to matrix isolation studies of carbon. However, we kept the mysterious 'camel hump' features in mind.

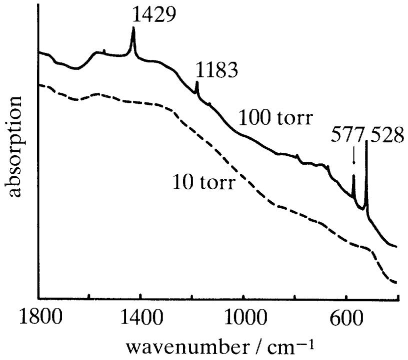

Figure 2. Absorption of carbon particles in the infrared. At elevated helium quenching gas pressures, there are four stronger lines emerging out of the continuum. Theory predicts precisely four ir-active fundamentals for a football structured C_{60} molecule and they should occur close to the measured positions. Such spectra gave us the first strong hint that we produced C_{60} in macroscopic quantities. Some of the tiny line features originate from the less abundant fullerent C_{70}.

3. Buckminsterfullerene

In the autumn of 1985 we read about the exciting C_{60}-Buckminsterfullerene discovery and about the ball proposal for its molecular structure (Kroto *et al.* 1985). Many theorists began to predict (among other things) its UV, infrared (IR), and Raman spectra. A remarkable result was that – for symmetry reasons – the infrared spectrum of football C_{60} should exhibit only four absorptions, two grouped at around 1600 cm^{-1}, and two grouped at around 600 cm^{-1} (see, for example, Weeks & Harter 1989). However, at this time the C_{60} molecules were only produced in cluster beams, i.e. in quantities insufficient for conventional optical spectroscopy or X-ray structural analysis. The football structure, even though 'too beautiful and perfect to be wrong' (Kroto 1992) remained a hypothesis.

In 1986 one of us (D. R. H.) began to consider that our camel hump carrier might possibly be due to the elusive buckminsterfullerene, and in 1987 a patent disclosure was submitted to appropriate channels of the University of Arizona. When we both met at an IAU Symposium in Santa Clara, California in summer of 1988, we discussed the case for C_{60} again. If the camel hump carrier is not 'junk' what else could it be other than C_{60}? Apart from a vague similarity between the camel hump features and the calculated uv spectrum of C_{60} (Larsson *et al.* 1987), however, the evidence was rather circumstantial. The few measured spectral data available on C_{60} did not support this idea (see Heath *et al.* 1986).

At the conclusion of the Symposium, we made new efforts to produce and investigate the camel hump soot. With the help of B. Wagner (in Heidelberg) and L. D. Lamb (in Tucson) we found the helium pressure to be the key parameter for producing camel hump features. Between 100 and 200 torr of helium the features appeared regularly, and we continued to use such pressures in all future work. In Heidelberg, the newly produced camel samples were studied with a very sensitive Fourier transform IR spectrometer. To our surprise, besides an intense continuum of regular graphitic smoke particles, four stronger line absorptions were clearly discernable, at frequencies very close to the positions predicted by vibrational theory for the football C_{60} (see figure 2). There was much excitement, since this implied that our samples not only contained C_{60}, but also that it was present in considerable quantities. We estimated the concentration as an order of a percent of the graphitic soot. However, the euphoria soon was followed by considerable concern. We still could not completely exclude the possibility that the IR lines were produced by contaminant, and we felt that such a sensational result, if true, had to be substantiated by additional experiments.

4. Fullerites

As part of his thesis work K. Fostiropoulos, in Heidelberg, investigated the effects of possible soot contamination and used much cleaner conditions and procedures than used previously. The appearance of the camel hump was not affected. With slightly renewed confidence we presented a paper of this observation at a workshop on interstellear matter in September 1989 (Krätschmer *et al.* 1990*a*). In a final attack on the problem (junk or not) Fostiropoulos and one of us (W.K.) succeeded in producing carbon rods that were sintered from 99% isotopically enriched ^{13}C powder. Shortly afterwards (late February 1990) the rods were successfully evaporated and the valuable smoke collected. We observed precisely the lineshifts in the IR spectrum of the soot as expected for pure carbon, while the UV spectrum remained unchanged. The conclusion was now clear: the carrier of the mysterious UV and IR lines had to be a pure carbon molecule and not junk. This and some additional results were written up and submitted for publication (Krätschmer *et al.* 1990*b*). From this time on, we coordinated our efforts and kept in constant contact by mail, fax and telephone. There was also more urgency to our work, since we noticed we were not alone in pursuing C_{60} and soot. The Sussex-group had succeeded in producing camel samples and confirmed that it exhibited four IR lines. There were also rumours that a group at IBM in San Jose was working in this direction.

At the end of April 1990 we were contacted by W. Schmidt, a chemist we knew from his work on interstellar dust and polycyclic aromatic hydrocarbon molecules. Following his suggestions, we achieved two important successes in May 1990 leading to a separation of the C_{60} from the soot. First, we discovered that heating the soot to *ca.* 500 °C *in vacuo* or in an inert atmosphere results in sublimed coatings which show all the absorption features of the camel samples, without any soot continuum. Second, we observed that the coatings dissolved in benzene, toluene, and various other non-polar solvents. This finding led naturally to the method of separating the insoluble graphitic grains from the fullerenes by simply washing the fullerenes out of the soot sample. A drop of the concentrated solution, dried on a microscope slide, provided the first view of the crystals of this new form of carbon, as shown in figure 3. One very easily obtains thin flake-like crystals which are ideally suited to electron diffraction studies. The crystal powder was subjected to X-ray Debye–Scherrer analysis. Mass spectrometry confirmed that the separated material consisted of C_{60} with a few percent C_{70}. From the diffraction data we deduced that the fullerene molecules form a lattice according to the close packing of spheres. The nearest neighbour distance turned out to be about 1 nm, which is close to the distance expected for the spherically shaped C_{60}, when a reasonable extension of the π-electron cloud is taken into account. These data, which strongly support the football structure of C_{60}, were submitted to *Nature* and published in September 1990 (Krätschmer *et al.* 1990*c*).

It was clear that for the first time we had produced a brand new crystalline form

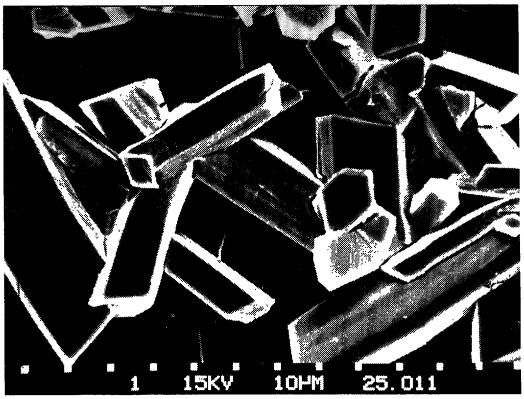

Figure 3. One of the first scanning electron microscope pictures of fullerene crystals, obtained by drying from a benzene solution. The picture was taken by K. Fostiropoulos. The rod-shaped crystals consist of C_{60} with a small admixture of C_{70} and traces of solvent molecules.

of pure carbon and that the molecular crystals are composed of the long-sought spherical molecule C_{60}, buckminsterfullerene. For this reason we suggested the special term *fullerite* for the solid.

In addition we had devised a method for making copious quantities of this molecule, discovered in 1985 but never previously made in sufficient quantity to be seen. In the work following our first studies, many other groups used the new material and soon it became proven beyond any doubt that the proposal by Kroto and co-workers of a ball shaped C_{60} molecule was correct. More recently, fullerene researchers started to study not only the soluble fractions of the soot, i.e. C_{60}, C_{70}, and the other larger stable 'magic number' fullerenes, but also they have looked very closely at the soot collected from various parts of the vacuum chambers and from the unevaporated residuals on the graphite electrodes. They found a variety of closed caged structures: round, elongated, tube-like, single-layered or nested within each other. It appears that a large scientific and technological playground with nicely shaped nano-toys has been opened. The challenge is to work out how to separate all these molecules, determine their properties and, finally, find uses for them.

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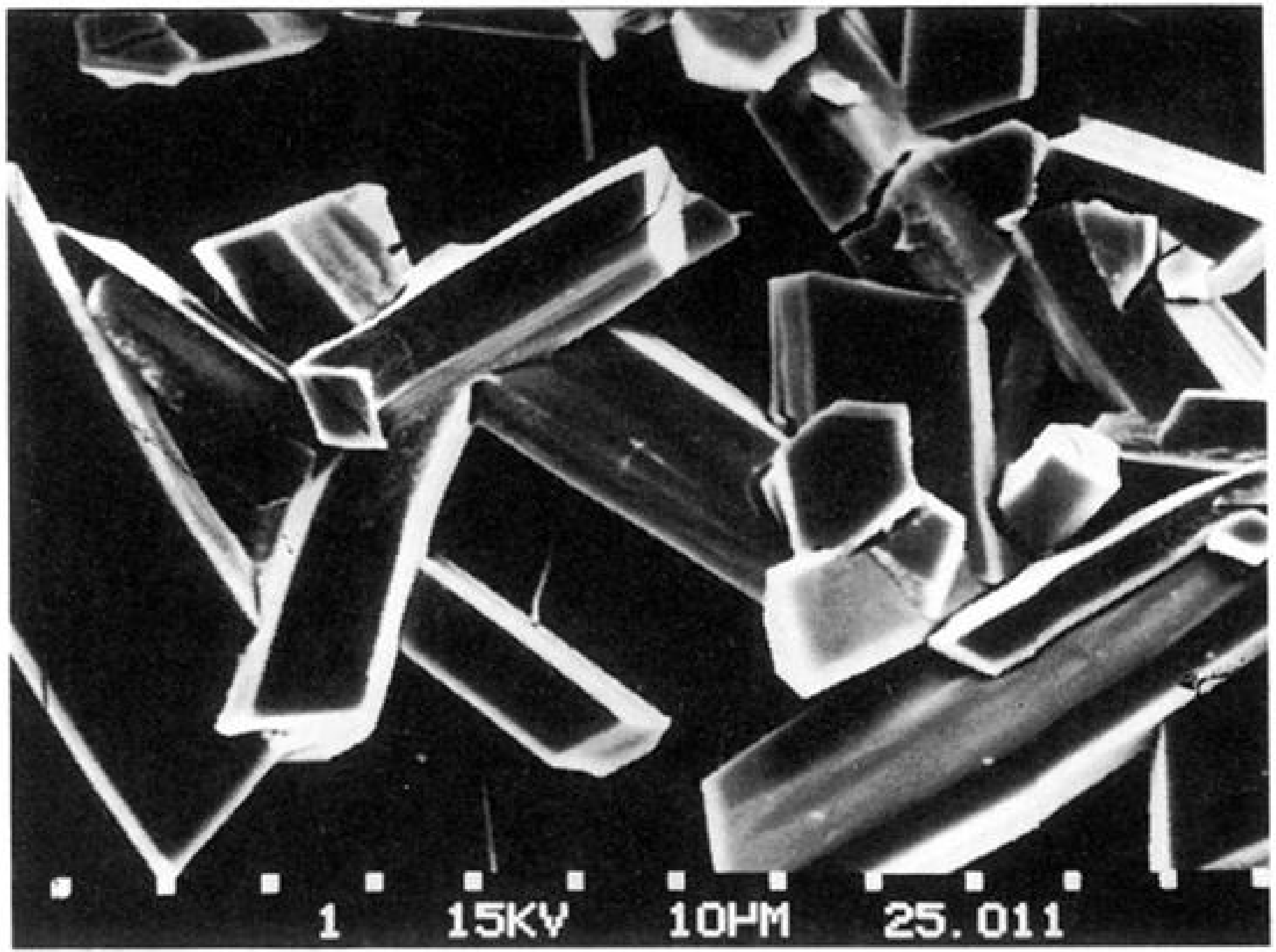
Discussion

M. Jura (*University of California, U.S.A.*). There has been a report from a shuttle experiment that the UV polarization of the interstellar extinction continued through the 220 nm feature. Is this consistent with the notion that since you would expect the polarization produced by grains, for example picket-fence molecules, to be lined up by a magnetic field, how can this occur if the molecules are spherical?

W. Krätschmer. That would not support our picture of course, but I wonder if this is really the case. There have been reports to the contrary, so we are waiting for the decisive result.

S. Leach (*Observatoire de Paris – Meudon, France*). Looking at hydrogen deficient stars, the peak in the UV spectrum shifts to about 250 nm. Do you think this means that hydrogen is involved in some way with the 230 nm peak?

W. Krätschmer. This may be the case. A shift can be produced in many ways. I have assumed the particles are small compared with the wavelength. If the particles are large, then you can have the peaks shifted to a longer wavelength. So one can assume that outflows from stars may consist of larger particles. On the other hand, one can not exclude the presence of hydrocarbons, for which there is plenty of evidence. But the spectra of these compounds are not well known as yet. These kinds of particles are all possible, and I would say that certain amounts of hydrogen will be involved, as hydrogen is everywhere. But, obviously the amount is restricted to such an extent that it has no major influence on the optical properties.



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