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Laser deposition of carbon clusters on surfaces: A new approach to the study of Fullerenes

Gerard Meijer and Donald S. Bethune^{a)}

IBM Research Division, Almaden Research Center, San Jose, California 95120-6099

(Received 7 August 1990; accepted 31 August 1990)

We have accumulated large pure carbon clusters (Fullerenes) on a surface. These clusters were produced by laser vaporization of graphite in a static rare-gas atmosphere. Their presence on the surface was confirmed by an isotope scrambling experiment using a laser-desorption/laser-ionization mass spectrometric detection scheme.

Since they were first observed experimentally by groups at Exxon and Rice several years ago,^{1,2} the large pure carbon clusters known as the Fullerenes ($C_{2n}, n \geq 16$) have fascinated scientists from disciplines as diverse as quantum chemistry, combustion science and astrophysics. Particular attention has been paid to C_{60} , often strikingly prominent as an ion in mass spectra of these clusters, which is proposed to have the structure of a soccerball—a hollow sphere made up of 20 hexagons and 12 pentagons, arranged as a truncated icosahedron.² This delightful prediction has inspired a great deal of theoretical work on the electronic, vibrational and rotational energy levels of such a molecule.³⁻⁶ Experimentalists have also expended considerable effort to obtain chemical and spectroscopic evidence that would bear on this prediction.⁷⁻¹⁰ To date, however, the search for spectroscopic data for the Fullerenes has yielded only a single electronic absorption feature for C_{60} complexed with either benzene or dichloromethane observed near 386 nm by Heath *et al.*¹¹ No direct structural evidence has been obtained. The difficulty in obtaining such evidence is related to the fact that from the beginning these species have been created and observed as transient species, available only at low densities for times of the order of 10 s^{-4} . For the ionized clusters, ICR techniques have extended the time available for experimentation to minutes or more, but the densities still remain too low for conventional spectroscopy.

In thinking about new ways to obtain information about these species, we were struck by the fact that the chief claims made for C_{60} , for example, are that it is very stable and remarkably chemically inert. If these claims are correct it should be possible to accumulate samples of Fullerenes.

In this communication we report direct evidence that Fullerenes can be trapped, stored and accumulated on surfaces. In addition, we show that they can subsequently be returned to the gas phase for study with mass and optical spectrometric techniques. Our experiments indicate that Fullerenes can be produced and accumulated in sufficient quantity to make them accessible to more conventional chemical and physical separative and analytical techniques.

In our approach, the creation and detection of the Fullerenes take place in two different pieces of apparatus. Creation and accumulation of the carbon clusters is accomplished by ablation of graphite (Pure Tech, 99.99% C) using

pulses of focused 532 nm light from a doubled Nd:YAG laser under a static Argon atmosphere at a typical pressure of 500 Torr. The base pressure of the diffusion pumped deposition chamber is $\sim 3 \times 10^{-7}$ Torr. A deposition substrate is placed parallel to the graphite face and approximately 1 cm away. The nature of the substrate does not seem to be important, and various materials were used, including copper, gold, and suprasil fused silica. After deposition the substrate was removed from the chamber. No attempt was made to prevent exposure of the sample to room air. The surface was observed to have a distinct dark gray haze, darkest opposite the irradiated spot on the graphite.

The substrate with the deposited clusters was then loaded into a separate apparatus and analyzed using the technique of laser desorption followed by jet-cooling mass spectrometry. In this technique, molecules originally adsorbed on the surface are brought intact into the gas phase using laser desorption, and are entrained in a pulsed supersonic gas expansion. This cools the molecules and transports them into a high vacuum region where they are photoionized between the extraction plates of a linear time-of-flight mass spectrometer. The spectra are displayed on a digital oscilloscope (LeCroy 9400) and read out by an IBM PC. A mass resolution $M/\Delta M = 300$ is obtained. The apparatus used has been described fully in recent publications.¹²⁻¹⁴

A typical mass spectrum of the deposited material is shown in Fig. 1. The sample was made using 6×10^3 ablation pulses (200 mJ) focused by a cylindrical lens ($f = 50 \text{ cm}$) to a sharp line on the graphite target. In this case a copper bar was used as a deposition substrate. In the detection apparatus desorption from the bar was induced by a $60 \mu\text{J}$ KrF (248 nm) laser pulse, loosely focused in a $\sim 0.25 \text{ mm}$ diameter spot. Under these conditions one desorption pulse basically depleted all of the deposited material in the irradiated area. For multishot averaging the sample bar was translated between desorption pulses. Argon with an 8 atm backing pressure was used as the carrier gas, and the gas jet with the entrained desorbed material was skimmed and subsequently ionized by an ArF laser pulse (193 nm, $\sim 180 \mu\text{J}$ in a 1.4 mm diameter spot).

The most striking feature in Fig. 1 is the dominance of the C_{60} and C_{70} positive ion peaks. Both peaks are singular in this spectrum, in that very few Fullerenes smaller than C_{60}

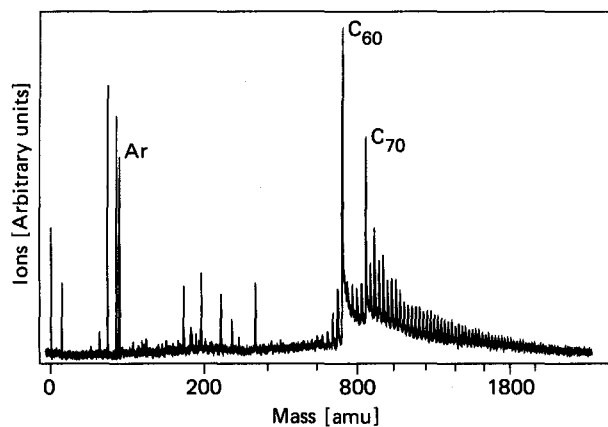


FIG. 1. Time-of-flight mass spectrum of laser deposited carbon clusters taken using the laser desorption jet-cooling detection apparatus. The horizontal axis is linear in time of flight and the corresponding (nonlinear) mass scale is indicated.

are present, while even clusters above C_{70} appear with higher intensities. In fact, these latter clusters are even more abundant than they appear since they are detected with reduced efficiency; both the channelplate quantum efficiency and the transmission of the TOF mass spectrometer are reduced for higher masses (no deflection voltage to correct for the beam velocity was used). The C_{60} signal corresponds to $2\text{--}4 \times 10^4$ ions per shot being produced between the extraction plates of the TOF mass spectrometer. This spectrum was averaged over forty shots, although mass spectra taken with a single shot looked essentially identical. The apparent continuum of masses that underlies the Fullerenes seems to be real and to have interesting structure to the high mass side of both the C_{60} and C_{70} peaks. Its origin is unknown at this time, but the exposure of the sample to air may lead to reaction of molecules containing noncarbon atoms with some of the deposited clusters.¹⁵

The various mass peaks in the 100–400 amu range are artefacts indicating some surface contamination due to residual low vapor pressure organics in the detection apparatus from earlier studies. The peaks at still lower masses are also unrelated to the deposited carbon sample (Ar^+ , Ar^{++} , Al^+ , H^+), with the possible exception of the peak at mass 36, which may be due to C_3 . Stray light from the ArF laser reaches the channelplate and causes the peak at zero mass.

So far we have assumed, based on our experience with stable organics using similar low desorption laser pulse energies in our detection apparatus, that we only sample species already present on the surface. It might be argued, however, that the Fullerenes arise in gas phase reactions which occur *after desorption* into the high pressure inert gas pulse. Although no carbon clusters were produced when a graphite target was put into the detection machine and used as a sample, one might still argue that the laser deposition process produces some special precursor material from which the

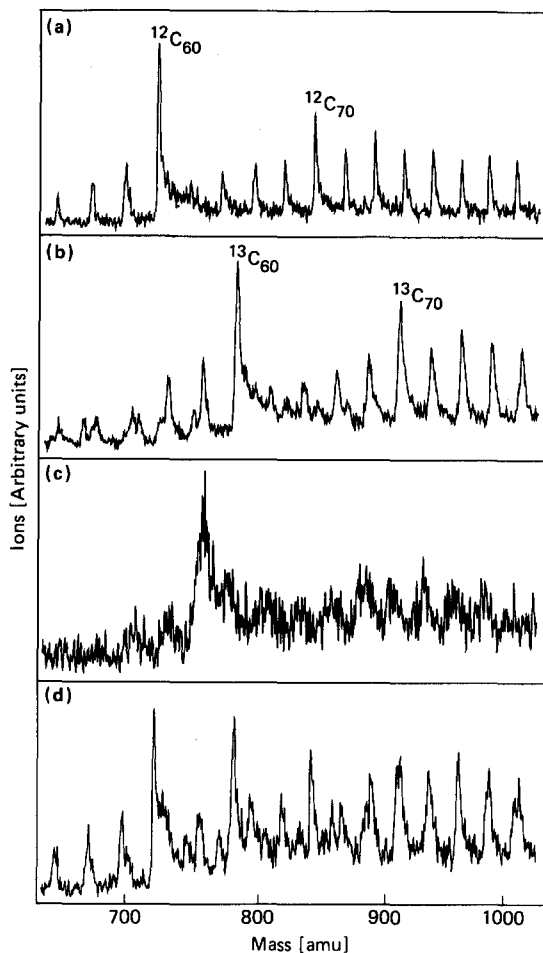


FIG. 2. Time-of-flight mass spectra of laser deposited carbon clusters produced from (a) pure ^{12}C (b) pure ^{13}C and (c) a 1:1 mixture of ^{12}C and ^{13}C . Spectra are averaged over 40 shots. Spectrum (d) is obtained from a sample bar on which material from isotopically pure ^{12}C and ^{13}C was laser deposited in the sequence $^{13}\text{C}/^{12}\text{C}/^{13}\text{C}/^{12}\text{C}$.

Fullerenes can be formed in the detection apparatus. Since we estimate the amount of carbonaceous material desorbed per shot in this machine to be on the order of a nanogram, the resulting densities are considerable and this possibility cannot simply be dismissed without serious consideration.

To distinguish between these two possibilities for the production of the Fullerenes, we have carried out an isotope scrambling experiment. We used samples made from isotopically enriched amorphous carbon powder (Isotec, 99.9% ^{12}C and 98.1% ^{13}C). The powders were held in small cavities bored in stainless steel cylinders, closed with cover plates with 1.5 mm holes through which 10 mJ of green light was focused. Copper bar deposition substrates were held about 1 cm away opposite the cover plate holes. First, deposits were made on two different sample bars using pure ^{12}C and pure ^{13}C powder targets. The mass spectra obtained from these bars are shown in Figs. 2(a) and 2(b), respectively. The C_{60} and C_{70} mass peaks dominate in both cases, shifted in the case of ^{13}C from 720 to 780 and from 840 to 910 amu, respec-

tively. The ^{13}C -cluster peaks are broadened slightly by the residual ^{12}C .

We then made an approximately 1:1 mixture of the two isotopes and made a third sample by laser evaporating this mixed powder. As shown in Fig. 2(c), the mass spectrum obtained from this sample has a broad peak at mass 755 amu, roughly centered between 720 and 780 amu. Notice also that no pure isotopic cluster peaks can be discerned. These facts are consistent with the interpretation that the peak at 755 amu, for example, is due to C_{60} clusters, with a statistical distribution of isotopes. If these clusters are built up from randomly selected monomers, the expected peak width would be about 10 amu, and the pure isotopic clusters would be sixteen orders of magnitude less abundant than the cluster with equal numbers of ^{12}C and ^{13}C atoms. But this interpretation leaves open the key question: Where are the clusters being made? To answer this question we deposited material from isotopically pure ^{13}C and ^{12}C powders in the sequence $^{13}\text{C}/^{12}\text{C}/^{13}\text{C}/^{12}\text{C}$ on a single sample bar before moving it into the detection apparatus. The mass spectrum of this sample bar would be expected to have very different characteristics depending on whether the Fullerenes are made initially in the deposition chamber or later in the detection machine. If the Fullerenes form in the deposition chamber from the pure isotopic vapors, we expect to find a mixture of pure isotopic clusters coexisting on the surface. On the other hand, if Fullerenes form in the desorption plume in the detection machine from 1:1 mixed isotope precursor material, we expect to see mixed isotope clusters similar to those seen in Fig. 2(c).

The mass spectrum we actually obtained is shown in Fig. 2(d). The pure isotope cluster peaks corresponding to $^{12}\text{C}_{60}$, $^{13}\text{C}_{60}$, $^{12}\text{C}_{70}$, and $^{13}\text{C}_{70}$ are immediately apparent, and the spectrum seems to consist entirely of pure isotopic clusters made from either ^{12}C or ^{13}C . Although this spectrum was made by averaging 40 shots which sampled an area of $1.2 \times 2 \text{ mm}^2$ on the sample bar, it should be emphasized that even for single shots the signal-to-noise ratio was sufficient to identify all four of the main pure isotope cluster peaks. This is conclusive evidence that *the Fullerenes were formed in the deposition chamber, were accumulated on the surface, and were already present when the sample was introduced into the detection machine.*

Having established that Fullerenes are laser deposited on the surface, it is of practical interest to try to estimate in what quantity they are present. We noted above that $2\text{--}4 \times 10^4 \text{ C}_{60}$ ions per shot are produced under the conditions relevant to Fig. 1. This can be related to the C_{60} density on the surface by using the apparatus efficiency for the detection machine as measured for perylene,¹⁴ and assuming an

ionization efficiency P_i for C_{60} . This yields a surface density of $(2\text{--}4 \times 10^{12}/P_i) \text{ C}_{60}$ molecules/cm². An upper limit of $P_i = 0.02$ can be deduced from the ionization data given by Cox *et al.*¹⁰ which implies a lower limit for the surface density of 10^{14} molecules/cm² (120 ng/cm^2).

To summarize, we have proven that Fullerenes can be laser deposited on a surface. This development opens new paths to knowledge about these fascinating species. For example, our detection machine itself, although used here only as a mass spectrometer, enables spectra of internally cold molecules to be obtained, starting with sub μgrams of material.¹⁴ Beyond that, the fact that significant quantities of Fullerenes can be accumulated may soon make them accessible to more conventional chemical and physical separative and analytical techniques.

Note added in proof: Since this work was submitted, Krättschmer *et al.*¹⁶ have reported production, purification, and characterization of $\sim \text{gm}$ quantities of C_{60} .

ACKNOWLEDGMENTS

We would like to thank Mattanjah S. de Vries, Heinrich E. Hunziker, and H. Russell Wendt for making their laser-desorption jet-cooling mass spectrometer available to us, and for their enthusiastic support and encouragement during the course of this work.

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